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AMONG the papers to appear in early issues of the *Journal* are the following:

"Fabric of Quartzites near Thrust Faults." By ROBERT BALK

"A High-Level Boulder Gravel East of the Laramie Range, Wyoming." By J HARLEN BRETZ and LELAND HORBERG

"Selenomorphology." By ALICE COLEMAN

"Late Cenozoic Marine Glacial Sediments and Marine Terraces of Middleton Island, Alaska." By DON J. MILLER

"Chemical Composition of Pre-Cambrian Slates, with Notes on the Geochemical Evolution of Lutites." By R. H. NANZ, JR.

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"Pleistocene Evolution of the Ohio and Wabash Valleys." By WILLIAM J. WAYNE

"Periglacial Frost-Thaw Basins in New Jersey." By PETER E. WOLFE

"The 10 Per Cent $CaAl_2Si_2O_8$ Plane in the System $CaSiO_3$-$Ca_2Al_2SiO_7$-$NaAlSiO_4$-$CaAl_2Si_2O_8$." By HATTEN S. YODER, JR.

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SMITH, A. V. (1926) Discovery of fish remains in Ordovician rocks of the Black Hills (abstr.): Geol. Soc. America Bull. 52, p. 27.

——— and DUNSANY, A. J. (1929*a*) Early Ordovician faunas of South Dakota: U.S. Geol. Survey Bull. 444, pp. 1–76.

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THE JOURNAL OF GEOLOGY

July 1952

PLEISTOCENE DRIFT SHEETS IN THE LETHBRIDGE REGION, ALBERTA, CANADA[1]

LELAND HORBERG
University of Chicago

ABSTRACT

Three Pleistocene drift sheets exposed along the Oldman River Valley in southern Alberta are correlated tentatively with the Iowan and the Tazewell or Cary substages of the Wisconsin glacial stage. The "interglacial" beds of previous writers (here named the "Lenzie silt") are considered to be proglacial lake beds deposited in front of the retreating Tazewell or Cary ice sheet. An important retreat and readvance of the ice to the position of the Lethbridge moraine is evidenced within the area. The Saskatchewan gravels, which underlie the drift sheets, are believed to be nonglacial in origin and probably preglacial in age. As such they cannot represent a pre-Kansas "Albertan" stage of glaciation, as was proposed by Dawson.

INTRODUCTION

The stratigraphic interpretations of the Pleistocene drift sheets of the Alberta plains have depended largely on regional relations to drifts to the south and east and on the widespread occurrence of a deposit of stratified silt between "upper" and "lower" tills. The silt generally has been considered to be nonglacial in origin and to record a pre-Wisconsin interglacial stage (table 1). Dawson and McConnell (1895), on the basis of the "interglacial" beds, correlated the "lower" till with the Kansan drift of the Mississippi Valley and proposed that the underlying Saskatchewan gravels represented a pre-Kansan glacial stage, the "Albertan." Later the term "Albertan" was replaced by "Nebraskan" as the name for the earliest glacial stage in North America. The present paper bears directly on the "Albertan problem" in its primary concern with the origin and stratigraphic significance of the "interglacial" beds. It proposes (1) that the "interglacial" beds are proglacial lake deposits of Wisconsin age and (2) that the till sheets above and below are also of Wisconsin age.

Manuscript received June 7, 1951.

The Pleistocene sections, which form the basis of the present study, are exposed along the Oldman River in southern Alberta in an area extending from the foothills of the Rocky Mountains eastward for 90 miles onto the Great Plains (fig. 1). The important sections described by previous writers near Macleod, Lethbridge, Driftwood Bend, and Wolf Island occur within the area. Canadian sectional maps—Lethbridge (no. 15), Macleod (no. 65), and Medicine Hat (no. 66)—were used as a base.

The field study, which occupied four weeks of the summer of 1950, involved areal mapping and reconnaissance and the examination of about 35 Pleistocene sections.

PREVIOUS STUDIES

The previous interpretations which directly concern the problems of the Lethbridge region are summarized in table 1. Dawson and McConnell's pioneer investigations (Dawson, 1885, 1890, 1891, 1895; Dawson and McConnell, 1895) clearly distinguished the four major units in the section and recognized the pre-Kansan "Albertan" drift represented by the Saskatchewan gravels in the plains and early mountain drift near the Rocky Mountains (table 1; fig. 2). This interpretation of the Saskatchewan gravels was rejected by Calhoun (1906, pp. 49–52, 57), who concluded that the gravels were nonglacial and represented deposits reworked from Tertiary gravels occurring at higher elevations. Similar conclusions were reached by Alden and Stebinger (1913), and, soon after, the term "Albertan" was discontinued. Alden in his final report (1932, pp. 71–74) tentatively correlated the upper till with the late Wisconsin, the "interglacial beds" with the post-Iowan interstadial, and the lower till with the Iowan. Later studies of the Oldman River section by Johnston and Wickenden (1931) emphasized the nonglacial aspect of the "interglacial" beds and the weathered character of the upper part of the lower till. From this evidence they tentatively correlated the lower till with the Kansan and the upper

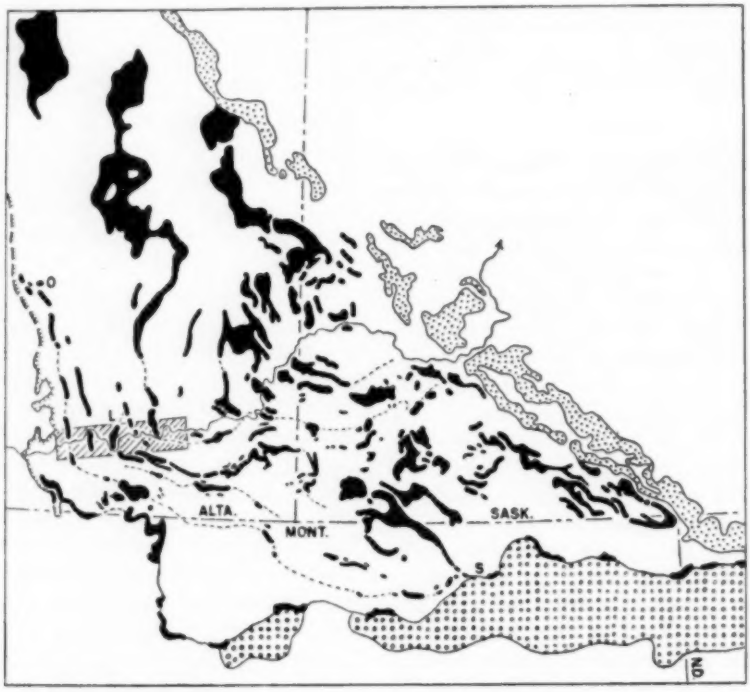


FIG. 1.—Map showing glacial deposits in Alberta and adjoining regions and the location of the area studied. Iowan (?) drift shown by circle pattern, Tazewell-Cary moraines in black, and Mankato Altamont moraine by dotted pattern. *O*, Okotoks moraine; *L*, Lethbridge moraine; *S*, moraine overlap near Saco, Montana.

till with the Iowan or Tazewell. Although the term "interglacial" is often a source of confusion, it seems clear that Dawson and McConnell and Johnston and Wickenden in the above papers had in mind a true interglacial stage and that Alden referred to an interval of indefinite duration.

All the previous workers with the exception of Calhoun, who did not examine the Oldman River sections, concluded that the upper till overlaps the lower till and extends westward to the mountain front or foothills area. Johnston and Wickenden (1931, p. 30) regarded the Okotoks moraine (fig. 2) as the probable western limit of the upper till. The present study indicates that overlap relations do not exist and that it is the lower till that extends westward to the mountain front (fig. 2).

CLIMATE AND SOILS

The climate is of continental type with a mean annual precipitation of about 15 inches and a temperature range from over 100° F. in summer to −50° F. in winter. Most of the precipitation occurs during the summer months (Mitchell and Moss, 1949, p. 433). The native vegetation is short- and medium-grass prairie. Pedocal soils prevail within the area, and

TABLE 1

PLEISTOCENE STRATIGRAPHIC INTERPRETATIONS

Stage or Substage	Present Paper (1952)	Dawson and McConnell (1895)	Alden (1932)	Johnston and Wickenden (1931)
Mankato		Upper boulder clay	Upper till	Upper till
Cary or Tazewell	Upper till			
	Lenzie silt			
	Lower till			
			Interglacial beds	
Iowan	Basal till		Lower till (?)	
Sangamon				Interglacial beds
Illinoian				
Yarmouth		Interglacial beds	Saskatchewan gravels	
Kansan		Lower boulder clay	Early mountain drift	Lower till
Aftonian				
Nebraskan		Saskatchewan gravels = Albertan drift		
Preglacial	Saskatchewan gravels			

the north-south boundary between Brown and Dark Brown (Chestnut) types is drawn just east of Lethbridge (Wyatt and Newton, 1928; Mitchell and Moss, 1949). These soils have profiles as shown generally in table 2.

REGIONAL RELATIONS

The area is situated just east of the Rocky Mountains in the northward continuation of the glaciated Missouri Plateau section of the Great Plains. Lying north of the continental divide between the Missouri and Saskatchewan drainage, the regional slope is eastward, and the Oldman River maintains a general easterly course within the area. Upland elevations adjoining the river decline from about 3,800 feet near the mountains to about 2,500 feet at the eastern edge of the area. The topography is in the stage of early youth, and its ma-

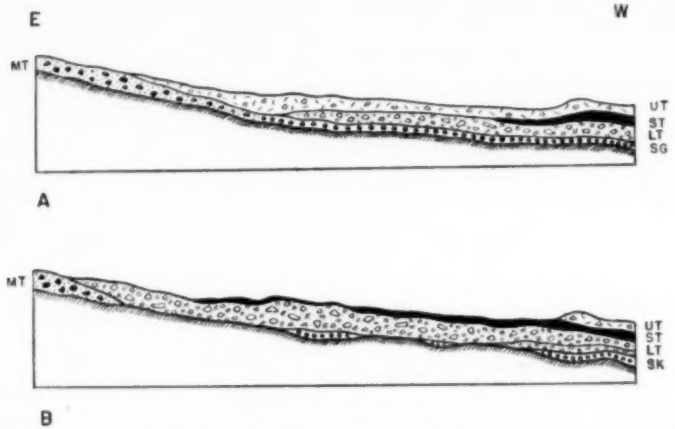


FIG. 2.—Diagrammatic cross-section of Pleistocene deposits between Lethbridge and the foothills of the Rocky Mountains, showing Pleistocene interpretations according to (*A*) Dawson and McConnell (1895, fig. 3, p. 45) and (*B*) the present paper. *UT*, upper till; *ST*, Lenzie ("interglacial") silt; *LT*, lower till, including basal till in *B*; *SK*, Saskatchewan gravels; *MT*, mountain drift. *SK* and *MT* in *A* represent the "Albertan" drift of Dawson and McConnell; *MT* in *B* is considered Wisconsin drift of mountain glaciers.

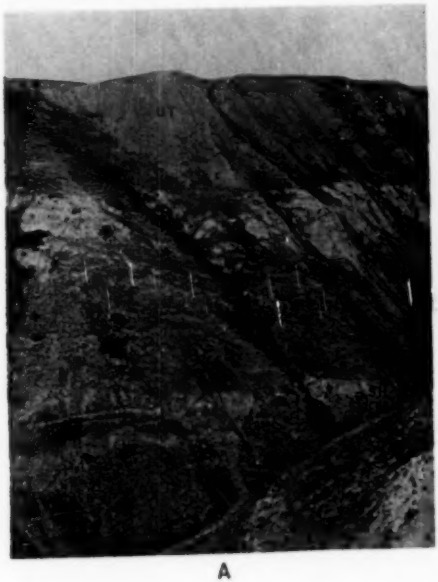
PLATE 1

A, Pleistocene section near east bluff of Oldman River, 4½ miles north of Lethbridge (no. *14*, fig. 2; center E. line, Sec. 30, T. 9 N., 21 W.) showing: upper till (*UT*), Lenzie silt (*L*), lower till (*LT*), basal till (covered), Saskatchewan gravels (*S*), and Cretaceous shale (*SH*).

B, Exposure in gully, 6 miles north of Lethbridge (no. *15*, fig. 2; center SW. ¼, Sec. 4, T. 10 N., 21 W.). Shows basal till (*BT*) with pebble zone at base, deformed Saskatchewan sand (*SS*) and gravel (*SK*), and Cretaceous shale (*SH*).

C, Pleistocene section along north bluff of Oldman River at Driftwood Bend (no. *17*, fig. 2; center Sec. 4, T. 12 N., 16 W.) showing: upper till (*UT*), Lenzie silt (*L*), lower till (*LT*), basal till (*BT*), and Saskatchewan gravels (*S*).

D, Type section of Lenzie silt along west bluff of Oldman River, ½ mile north of highway bridge at Lethbridge (no. *12*, fig. 2; SW. ¼ of SE. ¼, Sec. 11, T. 9 N., 22 W.) shows upper till (*UT*), Lenzie silt (*L*), and lower till (*LT*). Underlying basal till, Saskatchewan gravels, and Cretaceous shale are exposed but do not show in photo.



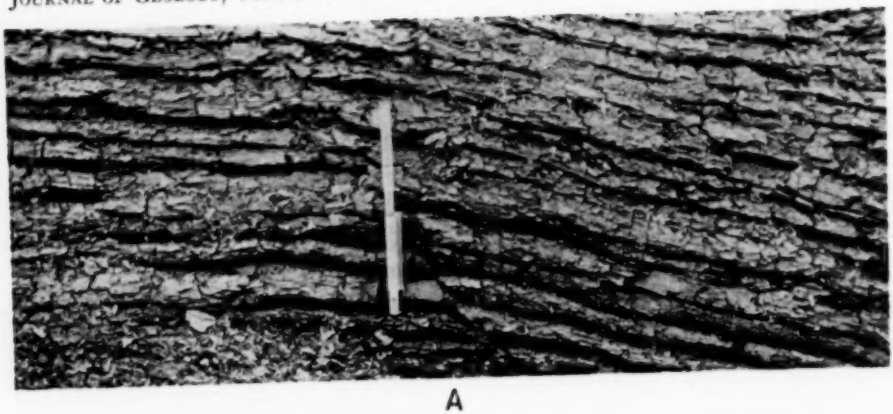
A

B

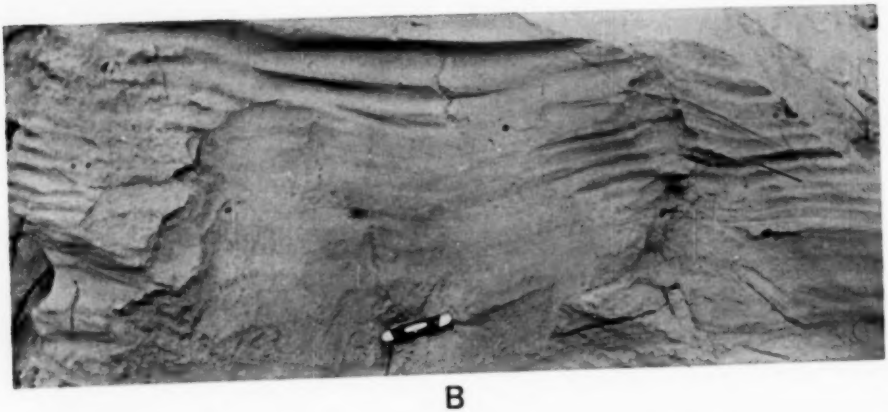
C

D

Pleistocene sections



A



B

C

Lenzie silt

jor elements include a series of discontinuous, broad, low end moraines and lacustrine plains (fig. 3). Below this constructional land surface, Oldman River and its major tributaries—Belly River, St. Mary River, and Bow River—are entrenched 150–250 feet in narrow, steep-sided valleys less than a mile in width. The valley sides, although slumped in many places, provide almost continuous exposures of the glacial deposits (pl. 1).

In terms of regional Pleistocene geology the area is situated in the outer western part of the moraine complex lying between the Altamont moraine on the northeast and the "early" Wisconsin drift margin to the west and south (fig. 1). Because the Altamont moraine is generally considered to be of Mankato age (Johnston and Wickenden, 1931, p. 36; Bretz, 1941, p. 34) and the "early" Wisconsin drift is bordered on the south by older drift of probable Iowan age (Alden, 1932, p. 69), the intervening moraines occupy a position comparable to the Tazewell and Cary drifts farther east.

The fact that the Keewatin ice sheet had to advance upslope into the headwaters area of the Saskatchewan drainage basin is a fundamental consideration in interpreting both the earlier and the later Pleistocene history of the region. As was recognized at an early date, this relation resulted in the formation of proglacial lakes at successively lower elevations as the ice withdrew from the region (fig. 3). The elevations of the lakes and the lake stages were determined by the elevations of a series of outlets by which the waters escaped around the margins of the ice and across sags into the Missouri drainage basin. The coulees formed by the outlet streams (Verdigris, Etzikom, Chin, and Forty Mile coulees, fig. 3) are striking features of the Albertan landscape and, as pointed out by Bretz (1941, p. 37), provide the best means available for the correlation of the discontinuous Alberta moraines.

TABLE 2

GENERAL SOIL PROFILE IN LETHBRIDGE REGION

Horizon	Description	Thickness (Inches)
A	Brown or dark brown, loose	2–6
B_1	Brown, compact, prismatic, non-calcareous	4–10
B_2	Gray zone of lime accumulation	10–18
C	Brownish gray, calcareous glacial drift	.....

PLEISTOCENE AREAL GEOLOGY

The moraines and Pleistocene lake basins within the area are shown in figure 3, which is a map based on earlier studies by Wickenden (undated map) and Bretz (1941, pl. 3, p. 52) with some revisions by the writer.[2] No attempt will be made to describe and interpret the

[2] The revisions include a more detailed mapping of the Lethbridge moraine and recognition of (1) the "Chin" moraine at the western border of the Lake Taber Basin, (2) the moraine northwest of Wolf Island, and (3) the southward extension of the Buffalo Lake moraine.

PLATE 2

A, Varved clay in Lenzie silt. East bluff of Oldman River, 5 miles southeast of Monarch (no. *6*, fig. 2; center NW. ¼, Sec. 26, T. 9 N., 23 W.).

B, Stratified silt with indistinct bedding, which is revealed on wind-etched surfaces. East bluff of Oldman River, 3 miles south of Lethbridge (no. *10*, fig. 2; N.E. ¼ of SW. ¼, Sec. 17, T. 8 N., 21 W.).

C, Colluvium (*C*) with blocks of Cretaceous sandstone and shale is interbedded in stratified, pebbly silt (*S*). *SC*, contorted pebbly silt; *LT*, lower till. Cut along Highway 3, 1 mile south of Monarch.

surface features in detail, but a chronologic summary is given in table 3. It should be noted, however, that the Lethbridge moraine marks a point of distinct readvance rather than a recessional halt and that the lake stages were interrupted by this event. This relation between the drift sheets east and west of the Lethbridge moraine is not apparent from the areal maps but can be established from the stratigraphic evidence given on following pages.

TABLE 3

SUMMARY OF PLEISTOCENE STRATIGRAPHY AND GLACIAL LAKE HISTORY

Substage	Stratigraphic Unit	Moraines	Proglacial Lakes (Elevation)*	Lake Outlets
Recent	Alluvium, colluvium, terrace deposits, volcanic ash, etc.			
Mankato	Unconformity			
	Upper silts		Lake Bassano (2,600)	Forty Mile Coulee
		Buffalo Lake moraine	Lake Taber (2,800)	Forty Mile Coulee
				Chin Coulee
	Upper till	"Chin" moraine	Lake Lethbridge (3,050)	Etzikom Coulee
		Lethbridge moraine		
Cary (?)	Unconformity	Possible buried moraines	Ancestral lakes in Oldman River basin	
	Lenzie silt		Lake Macleod (3,150)	Verdigris Coulee
		"Macleod" moraine	Lake Magrath stages (3,250–3,350)	Verdigris Coulee (south of area)
	Lower till	Okotoks moraine	Lake Cardston (3,900)	Lonely Valley (south of area)
		Earlier moraines	Earlier lake stages	
	Unconformity			
Iowan (?)	Basil till			
	Unconformity			
Preglacial	Saskatchewan gravels			
	Unconformity			
	Weathered zone on shale			

* Elevations of glacial lakes from Bretz (1943).

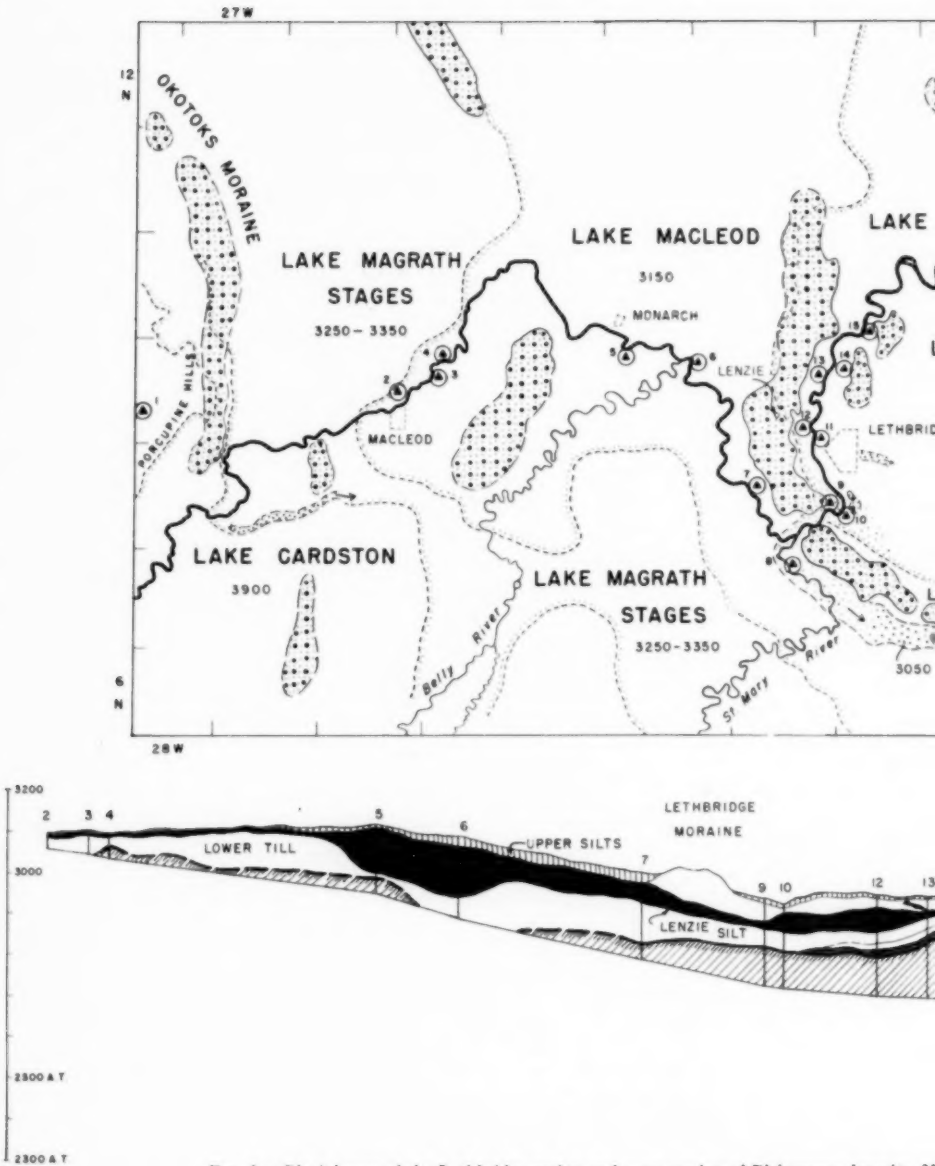
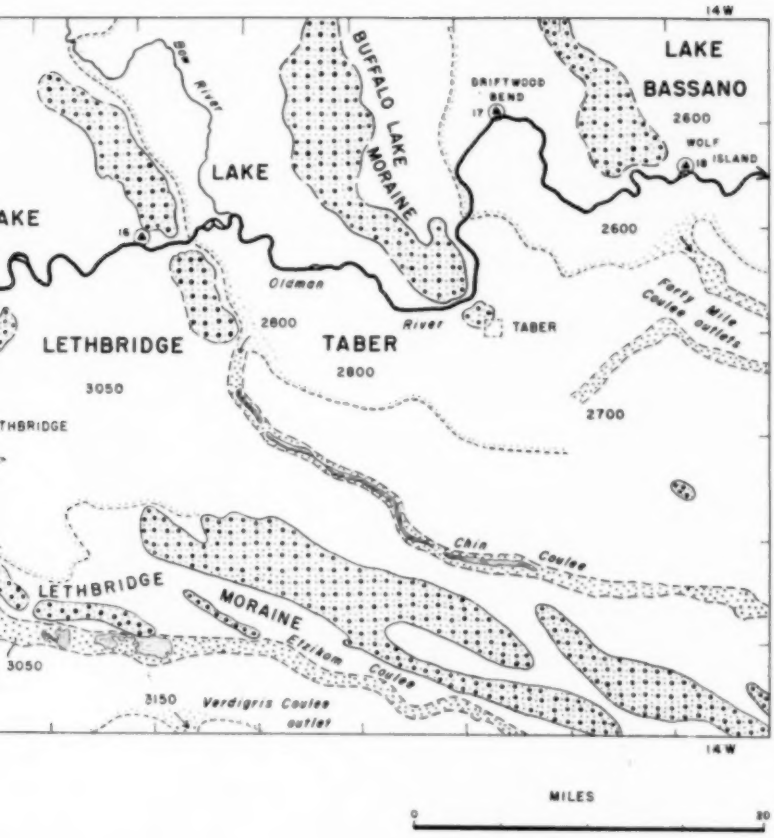
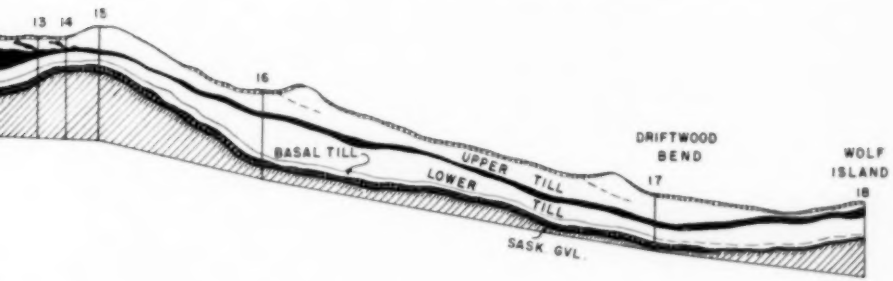


FIG. 3.—Glacial map of the Lethbridge region and cross section of Pleistocene deposits. N





its. Numbered triangles are Pleistocene sections. See appendix for detailed locations

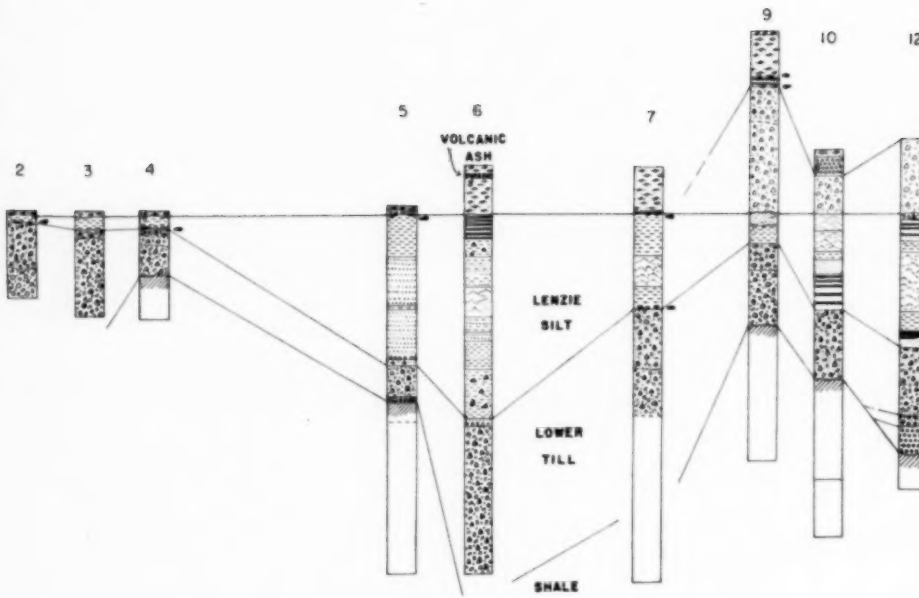
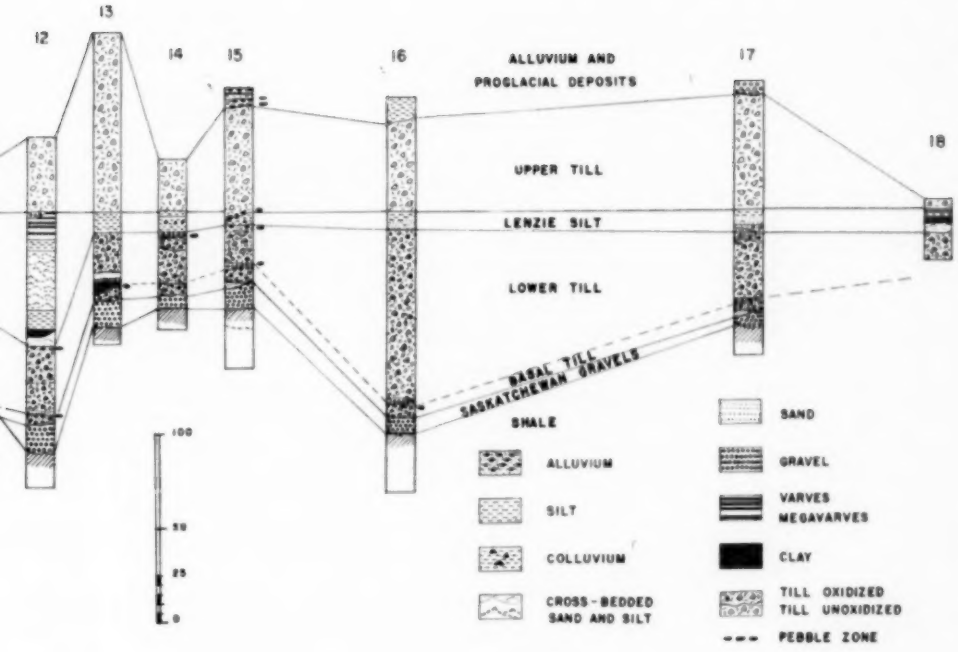


FIG. 4.—Pleistocene sections in the Lethbridge region. Locations are s



s are shown in fig. 2, and descriptions of selected sections are given in the appendix

STRATIGRAPHIC DESCRIPTION AND INTERPRETATION

GENERAL STATEMENT

The sections along the Oldman River provide exposures of the following units, from oldest to youngest: (1) Cretaceous bedrock; (2) weathered zone at the top of the Cretaceous beds; (3) Saskatchewan gravels; (4) basal till; (5) lower till; (6) Lenzie ("interglacial") silt; (7) upper till; and (8) upper silts, alluvium, and other deposits (fig. 4; pl. 1).

The upper Cretaceous formations consist largely of shale and sandstone with associated coal and include, from oldest to youngest, the Foremost, Oldman, Bearpaw, Blood Reserve, and St. Mary River formations (Russell and Lander, 1940, maps 565A and 566A). These formations are transected by an irregular erosional surface which determines the eastward regional slope of the present land surface and has a local relief of 100 feet or more. In places there is an earthy, oxidized, reddish-brown weathered zone at the top of the shale (nos. *5*, *11*, *15*, and *16*, fig. 4; and appendix).

SASKATCHEWAN GRAVELS

Description.—The Saskatchewan gravels, originally named the "South Saskatchewan gravels" (McConnell, 1885), p. 70), underlie the drift over a wide area in Alberta and have been described by numerous writers (see Williams and Dyer, 1930, pp. 69–76; Rutherford, 1937). In the Oldman River area the gravels are present at about half the sections studied, in thicknesses ranging from 1 foot or so up to 15 feet (pl. 1, *C*; fig. 4).

The gravels are composed of 50 per cent or more quartzite and chert with subordinate amounts of argillite, limestone, basic volcanics, and Cretaceous sandstone and shale (pebble count, fig. 6). Except for the local bedrock components, it is clear that the pebbles were derived from the mountains to the west, largely from Beltian and Paleozoic sources. Crystalline rocks and other rock types from regions to the east appear to be completely absent. The pebbles are well rounded and have an average diameter of about 2 inches, and a maximum diameter of about 8 inches. The gravels are nonindurated to partly indurated and have a silty gray-sand matrix. Layers and discontinuous lenses of sand similar to the matrix sand commonly occur with the gravel. The sand is medium-grained and composed largely of quartz, with minor dark minerals, micaceous minerals, and secondary calcite. Iron-staining is more pronounced than in gravels in the overlying drift. At one locality (sec. *16*, figs. 3 and 4) a 6-inch oxidized zone occurs at the top of the gravels. This zone, however, contains unweathered pebbles and has a fairly regular lower boundary, suggesting that the oxidation resulted from the action of confined ground water rather than from subaerial weathering.

The gravels commonly show uniform horizontal bedding, but in places they are imbricated and cross-bedded. Current directions indicated by the latter features were noted at several localities, but no consistent orientations were apparent.

In places the gravels clearly occupy bedrock channels which cross the present valley and are revealed by high bedrock exposures on either side of the channels. Also at certain localities, as along the highway at the west bluff of the river near Lethbridge, the basal contact can be seen to slope away from the valley. Hence there is no evident relation between the occurrence of the gravels and the present course of the Oldman River.

The gravels appear to be restricted to localities between Driftwood Bend (sec. *17*) and the mouth of St. Mary River (sec. *8*), but this distribution is probably of only local significance.

Genesis and age.—The available evidence indicates that the gravels are nonglacial stream gravels derived originally from the Rocky Mountains to the west, and as such they cannot be considered evidence of an "Albertan" stage of glaciation. It is uncertain whether they are early Pleistocene or late Tertiary in age or whether they are primary or reworked from older deposits, such as the Cypress Hills gravels. The complete absence of glacial characters, their stratigraphic position below the oldest known drift, their degree of oxidation, and the lack of relation to present drainage point to a late Tertiary age. The fact that they occur at lower physiographic levels than the high benches on which pre-Wisconsin mountain drift apparently was deposited, as emphasized by Alden (1932, p. 65), would indicate a mid-Pleistocene age. This argument, however, is based on an interpretation which considers the gravels to be younger than the plains physiographic surface, whereas it may be possible that the gravels are older and are truncated by the plains surface. There is some evidence of a period of denudation preceding the Cypress Hills and Flaxville cycles in Montana (Horberg, 1940, pp. 294–295), but numerous uncertainties are involved.

At present there appears to be insufficient evidence to decide the issue. It seems probable, however, that similar deposits of various ages are involved in the problem.

BASAL TILL

Description.—The basal till, which is a new unit differentiated from the "lower" till of previous writers, is recognizable in almost all sections near Lethbridge and to the east, but it appears to be absent in the western part of the area. It is distinguished from the overlying "lower" till by its prominent columnar structure, clayey composition, low pebble content, and the presence, at the top, of a persistent pebble zone which is commonly overlain by a basal sand and gravel of the lower till (pl. 1, *B*). Observed thicknesses range from 1 to 12 feet, the average being about 4 feet. In general, the basal till is very hard and dense, jointed, dark brownish gray in color, partly oxidized, calcareous, and chemically unweathered. At some localities the joints contain thin seams of calcite and gypsum. Zones of more intense oxidation at the top or bottom of the till in most places are related to associated sand and gravel beds and do not record subaerial weathering. In a few exposures the scattered pebbles in the till have a preferred orientation with their long axes horizontal (fig. 7, *E*).

The clayey character and dark color of the till indicate that it includes much fine material derived from the Cretaceous bedrock, and in places masses of dark-gray shale occur within the till. This, however, is not reflected in pebble counts (fig. 6, no. *11*), which show maxima of quartzite and chert from the underlying Saskatchewan gravels and minor percentages of local bedrock, limestone, and crystallines.

Age and correlation.—The pebble zone at the top of the till and the basal sand and gravel in the overlying drift record an interval of deglaciation following deposition of the basal till, but there is no evidence that it was of significant duration. The till is unleached, and, aside from oxidation, it has not been chemically altered. If a profile of weathering were ever present, it was removed before depo-

sition of the overlying lower till. Highly weathered glacial deposits of possible pre-Wisconsin age occur along Sage Creek in northern Montana (Alden, 1932, p. 74), but there is no evidence that the basal till represents such deposits.

The evidence available indicates an early Wisconsin age—Iowan or Tazewell. An Iowan age is tentatively proposed because of the presence of probable Iowan drift outside the limits of Keewatin moraines in northern Montana (fig. 1) and because of the fact that the basal till appears to represent the only clean-cut unit in the lower part of the section below the Lenzie silt. There are no recognizable breaks which can be ascribed to the four or more Tazewell-Cary moraines which lie to the southwest.

LOWER TILL

Description.—The lower till, which forms the main till body within the area, constitutes the surface moraines in the western part of the area and underlies the upper till in the eastern part of the area east of the Lethbridge moraine (figs. 3 and 4). It varies greatly in thickness because it forms the bulk of the fill by which irregularities on the bedrock surface are concealed. Measured thicknesses range from 20 to 90 feet, and it is probable that in places the maximum thickness is considerably more.

The till is similar to the basal till in being dense, hard, jointed, clayey, calcareous, and dark gray in color when unoxidized. It differs from it in being more pebbly and in not having such pronounced columnar structure. Fragments and large included masses of dark-gray Cretaceous shale are conspicuous in the till at certain localities. Jointing is conspicuous in the upper 10–15 feet and appears to be restricted largely to localities where the overlying upper till is present. The joints are clearly revealed by iron stains, and in most places they terminate at the top of the lower till.

Beds of sand and gravel occur commonly at the top and bottom of the till and locally within the till. At many places a pebble zone separates the till from the overlying silt.

Possible lacustrine deposits at the base of the till were noted at two localities (nos. *13* and *16*, fig. 3). The deposits consist of stratified clay, silt, and sand similar to the Lenzie silt. At locality *16* these silts are overlain directly by outwash gravel deposited by the advancing ice, which laid down the lower till. This relation suggests that the silts were deposited in a proglacial lake during the retreat of the ice sheet responsible for the basal till.

Pebble counts of lower till show that quartzite, chert, dark-colored limestone, and Cretaceous sandstone are dominant constituents (fig. 6). In the finer fractions a high content of Cretaceous shale is indicated by the dark color and clayey character of the till.

The upper part of the till is oxidized to a brown-gray or buff color to depths of 2–35 feet, the average being about 10 feet (fig. 4). It is probable that much of the oxidation is due to ground water moving downward from the overlying silts or upward from underlying sands and gravels rather than to subaerial exposure. These associated deposits above and below are oxidized, and in places (sec. *8*, fig. 4) there are both basal and upper oxidized zones in the till. It can be argued further that, because the oxidation is commonly controlled by joints and because the joints probably were produced in large part by the ice sheet that deposited the upper till, the oxidation occurred after deposition of the upper till and must be a ground-water ef-

fect. At any rate, there is no evidence, aside from oxidation, that suggests development of a profile of weathering. The till is calcareous up to the base of the overlying silts, and its pebbles are not chemically altered.

Age and correlation.—The lower till was considered to be Kansan by Dawson and McConnell (1895, pp. 65–66) and by Johnston and Wickenden (1931, pp. 35–39), whereas Alden (1932, pp. 71–74) tentatively correlated it with the Iowan (table 1). The pre-Wisconsin age assignment was based on the interpretation of the Lenzie silt as a true interglacial deposit and the occurrence of a possible weathered zone at the top of the till.

TABLE 4

SOIL PROFILE IN THE PORCUPINE HILLS

Horizon	Description	Thickness (Inches)
A	Brown, silty, loose, noncalcareous	6
B	Light-gray, compact, columnar structure, caliche at base	8
C_1	Dark-gray till with disseminated lime	12
C_2	Dark-gray till, calcareous, but with no visible lime	.....

The weathered zone was reported by Johnston and Wickenden from the Wolf Island locality (fig. 4, sec. *18*) and described as a "thick layer of brownish deeply weathered clay, containing peat and in places lignite" (1931, p. 33). The writer was unable to identify this layer but found the contact with the silts exposed at several places. The lower till immediately below the contact is unaltered by chemical weathering, calcareous, and only slightly oxidized. Fresh crystalline rocks occur within a foot of the contact. Concentrations of particles of carbonaceous shale and lignite from the Cretaceous bedrock are abundant in the Lenzie silts and clays at this locality and could resemble the deposit described above. Under normal conditions it would be unusual to find primary lignite in a weathered profile as young as Pleistocene.

Consideration of the weathering profile in more general terms raises the question of what a mature interglacial soil in this area would be like. If the interglacial climate were similar to the present, it might be anticipated that the depth of leaching would have little significance. However, it seems probable that there would be extensive B-horizon clay development and concentration of calcium carbonate. It is of interest that, although textural B-horizons generally have not been recognized in pedocal soils, Thorp and others (1949) recently have emphasized their significance. They recognize in the Prairie, Chernozen, Chestnut, and Brown soils the following subgroups: (1) *minimal* soils without well-defined B-horizons; (2) *medial* soils with moderately defined B-horizons; and (3) *maximal* soils with strongly defined B-horizons. In view of the mature interglacial soils of the Mississippi Valley, it is probable that interglacial soils in the Great Plains would be of maximal type and also have recognizable, strongly defined B-horizons.

In the Lethbridge region there is no evidence of a B-horizon or a zone of important lime enrichment. If such zones were ever present, they were removed by erosion before the deposition of the overlying silts at thirty or more exposures at which the contact was observed. Instead, the soil profiles on the lower till where it occurs at the surface west of the Lethbridge moraine are uniformly youthful, as shown in the Porcupine Hills (table 4; fig. 3, locality *1*). Although formed under semiarid climatic conditions, this profile more nearly resembles the youthful pro-

files on the Wisconsin drift sheets of the Mississippi Valley than the mature profiles of Illinoian and Kansan deposits.

Even more impressive is the evidence afforded by the youthful topography of the lower drift and associated lacustrine plains west and southwest of the Lethbridge moraine. Postglacial dissection is restricted in the main to the trenches cut by the major streams and to narrow gullied zones less than a mile in width which border them. Between the short gullies the constructional upland plain ends abruptly at the brink of the major valleys. The glacial topography, although modified by lacustrine deposition, is recognizable in both end-moraine and ground-moraine areas. Morainic knolls and basins are sharply defined in all the areas of end moraine and can be found at elevations up to 400 feet in the Porcupine Hills. Southwest of the area, moraine forms unmodified by lacustrine deposition are characterized by steep-sided knobs, ridges, and basins with hundreds of lakes and ponds (see the Cardston, Mountain View, and Pincher Creek quadrangle maps). The initial glacial forms are essentially unmodified over wide areas and, with due allowance to climatic factors, record a post-Iowan age. Certainly, if a decision were to be made on the basis of topography, a late Wisconsin rather than a pre-Wisconsin age would be favored.

The lower till is assigned to the Tazewell or Cary because of its youthful morainic topography and its geographic position between probable Iowan drift on the south and Mankato drift to the east.

LENZIE SILT

Definition.—It is here proposed that clays, silts, and sands which occur between the upper and lower tills of the Lethbridge region and at the surface west of the Lethbridge moraine, and which previously have been designated as "interglacial" beds, be named the "Lenzie silt." The name is taken from the railroad station of Lenzie along the Canadian Pacific Railway, 4 miles west of Lethbridge (shown on Macleod sectional map, no. 65). The type section is located on the west bluff of the Oldman River Valley, $1\frac{1}{2}$ miles southeast of Lenzie and 1 mile north of the highway bridge (SW. $\frac{1}{4}$ of SE. $\frac{1}{4}$, Sec. 11, T. 9 N., 22 W.; no. *12*, figs. 3 and 4; and appendix; pl. 1, *D*).

Description.—The deposit is composed dominantly of buff, stratified, calcareous silt and silty sand which from a distance has a loesslike appearance. In detail, however, it presents a variety of sediments, including the following main types which are recognizable in most thick sections: (1) papery, laminated, black or gray clay; (2) laminated clay and silt with laminations $\frac{1}{16}$ to $\frac{1}{2}$ inch thick (normal varves); (3) stratified silt and fine sand in layers 3–18 inches thick, with graded bedding (megavarves); (4) poorly stratified or unstratified loesslike silt; (5) silt and silty sand with foreset bedding or ripple cross-lamination (McKee, 1939, pp. 71–75); and (6) poorly sorted, till-like colluvium containing coarse fragmental material (pls. 2; 3, *A*). Detailed sections are shown in figure 4 and are described in the appendix.

Microscopic examination shows that the deposits in general are well sorted and consist largely of angular quartz with subordinate percentages of calcite, feldspars, ferromagnesian minerals, and micas and minor percentages of a variety of detrital minerals. Counts of pebbles from the silts (fig. 6) indicate a concentration of quartzite, but otherwise show all the rock types found in the tills.

Many of the unstratified silt beds have

the appearance of loess, but, when examined carefully in the field or under the microscope, sand and larger particles are found to be present. However, true loess deposits probably occur in places. Mechanical analysis of the upper silt at Driftwood Bend shows that it is similar to many loesses and differs markedly from the stratified silt (fig. 5).

type. At other localities lignite and carbonaceous shales from the Cretaceous bedrock and recent rootlets intruded along fractures and clay seams might be mistaken for organic material. In previous studies "lignite" and peaty material were reported from the silts at Driftwood Bend and Wolf Island (Dawson, 1885, p. 152*c*; Johnston and Wickenden, 1931, pp.

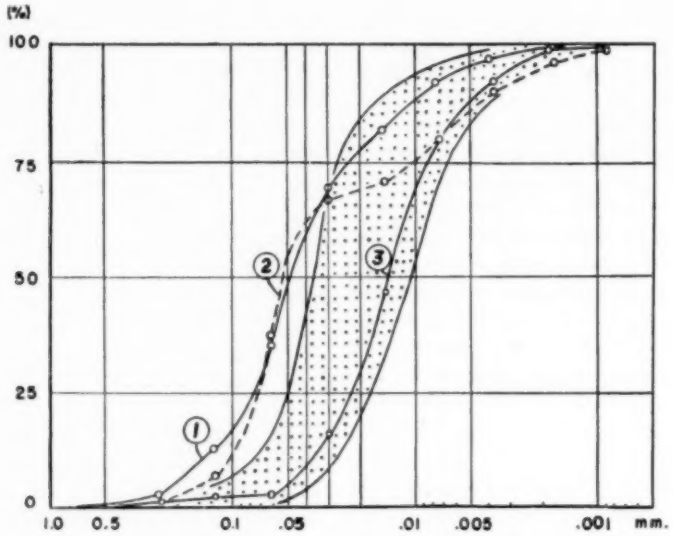


FIG. 5.—Cumulative curves of analyses of (1) volcanic ash from section 6 (fig. 2); (2) fluvial silt from section 18, Wolf Island (*dashed line*); and (3) loess from near section 17, Driftwood Bend. The stippled area shows range of analyses of loesses from other regions, based on analyses by Smith (1942), pp. 154–155 and Swineford and Frye (1945, p. 252).

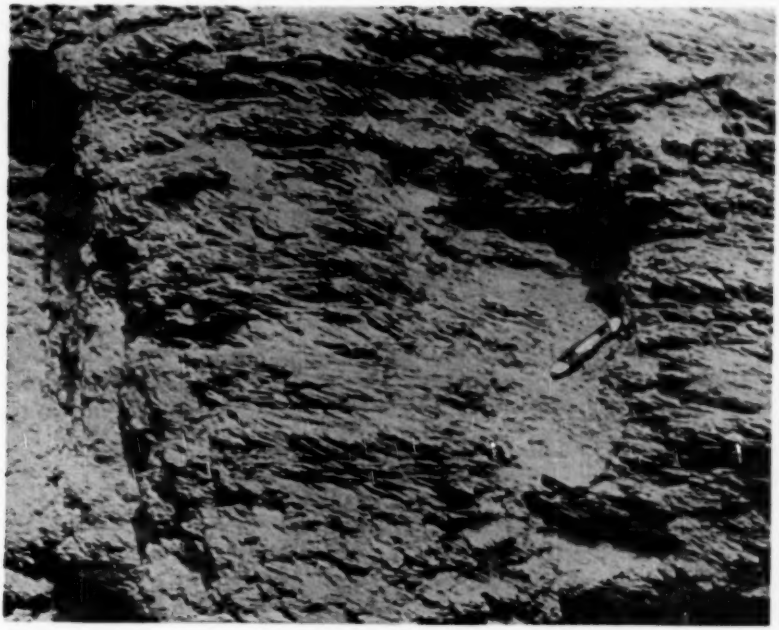
Primary organic material within the silt was definitely identified only at the Driftwood Bend locality (sec. *17*, fig. 4), where shell fragments, some identifiable as pelecypods, and possible plant fibers occur in a sandy, pebbly clay of colluvial

32–33), but no primary materials of this type could be found when the writer visited these sections. It seems possible, at least in Dawson's section at Wolf Island (1885, p. 153*c*), that Cretaceous beds were confused with the intertill silts be-

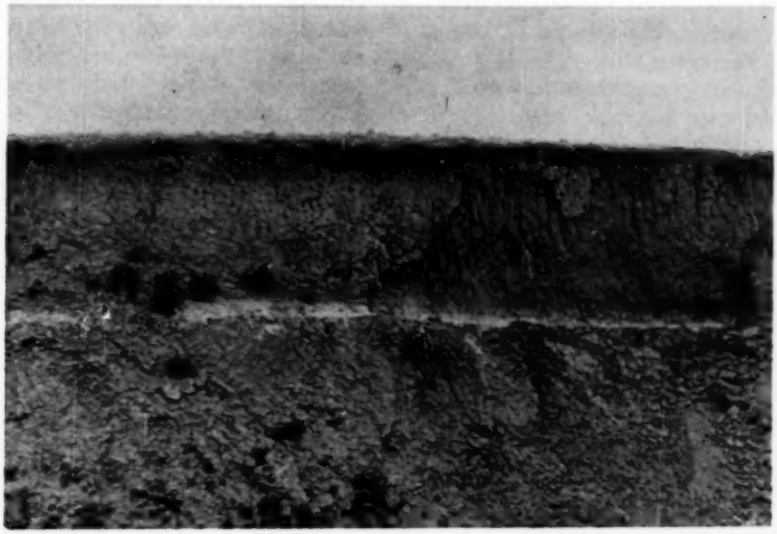
PLATE 3

A, Ripple cross-lamination in Lenzie silt. Highway cut at north bluff of Oldman River near locality *16*, fig. 2 (NE. ¼, Sec. 34, T. 10 N., 20 W.).

B, Volcanic-ash layer in postglacial alluvial silts. East bluff of Oldman River, 5 miles southeast of Monarch (no. *6*, fig. 2; center NW. ¼, Sec. 26, T. 9 N., 23 W.).

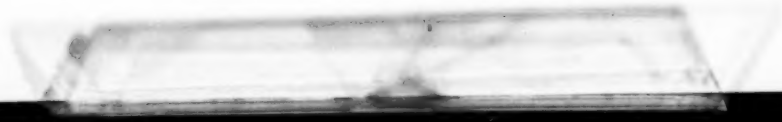


A



B

Ripple cross-lamination and volcanic ash



cause of the extensive slumping of the Pleistocene deposits. Dawson's section includes from top to bottom: 100 feet of "upper boulder-clay," 8 feet of "purplish sandy clay with ironstone and lignite," 15 feet of "lower boulder clay," 40 feet of Saskatchewan gravels and related sands and clay, and 10 feet of Cretaceous shale. In contrast, the writer found only a few feet, instead of 100 feet, of upper till underlain by 12 feet of megavarved silt, laminated clay, and ripple cross-bedded gray sand. Beds fitting the description of the "purplish sandy clay with ironstone and lignite," described by Dawson, occur in the underlying Cretaceous bedrock.

Repetition of similar beds in a graded series of sand, silt, and clay is a feature of most of the thicker sections (fig. 4, secs. *5*, *6*, *7*, *9*, *10*, and *12*). It does not seem possible, however, to correlate sequences of this type from one section to another.

Thickness and distribution.—The silts appear to be essentially continuous below the upper till in the eastern part of the area, although in some places they have been so disturbed and mixed with the till above and below that they form a zone rather than a distinct bed. West of the Lethbridge moraine they are undisturbed by ice-thrust and occur throughout the basin of Lake Macleod (fig. 3). They also should be present in the lake basins farther west, although few observations were made in these areas.

In the measured sections the silts range in thickness from about 5 feet to 113 feet. Variations in thickness within short distances are common, and at many localities it is possible to observe cross sections of thickened deposits in depressions resembling morainic basins on the surface of the lower till.

Colluvium.—Deposits of rudely stratified and poorly sorted materials occur at many places in the silts (fig. 4, secs. *5*, *6*, *14*, *15*, and *16*) and are believed to be the product of mass movements down slopes. The deposits are characterized by their discontinuous occurrence, composition of locally derived materials, and content of large fragments of fragile bedrock, such as shale, which normally do not withstand other erosive processes.

One of the best exposures of colluvium occurs along Highway 3, 1 mile south of Monarch (pl. 2, *C*), where 4–10 feet of till-like material are interbedded in lacustrine silt. The deposit is irregular in outline and consists of a confused mixture of clayey and sandy silt with imbedded angular fragments of local bedrock and pebbles from the glacial drift. Large tabular fragments of Cretaceous sandstone, one of them 5 feet in diameter, and masses of shale and lignite occur throughout the deposit. On the north side of the exposure a wedge of contorted pebbly silt intervenes between the colluvium and the overlying stratified silts.

At other localities the colluvium varies in the relative proportion of coarse and fine constituents.

Colluvium is being deposited at present along the steep valley slopes of Oldman River and its tributaries, but there is no evidence of important mass movements on the moraines and drift plains of the uplands. The slopes on the upland are stable at most places, and important climatic changes would be required to initiate extensive mass movements. It is believed, therefore, that the colluvial deposits on the lower till topography were formed under periglacial climatic conditions and represent solifluction and related debris accumulations. Deposits of this type are well known and are included under Bryan's (1946, p. 633) general term, "congeliturbate." In western Europe they commonly are designated as "head" (Dines, 1940) or "solifluction de-

posits" (Zeuner, 1945, p. 6), although numerous other terms have been applied.

Origin and age.—The Lenzie silt is regarded as primarily lacustrine, although fluvial, colluvial, and probable eolian deposits are included. Its occurrence at the surface in lake basins west of the Lethbridge moraine, the presence of varved and thinly laminated clays and silts, its resemblance to younger lake deposits in the Lake Lethbridge and Lake Taber basins, and its wide areal extent establish this conclusion. It was laid down as an off-lap deposit in proglacial lakes as the ice sheet that deposited the lower till withdrew from the area. Several facies seem to be represented, including: ice-margin, deep-water, near-shore, and deltaic lacustrine; slack water; floodplain; and colluvial. With a retreating ice margin and shifting lake outlets, conditions were favorable for repeated deposition of different facies at the same locality.

By this interpretation the silts are contemporaneous with the lower till and probably of Tazewell or Cary age.

UPPER TILL

Description.—The upper till includes the till of the Lethbridge moraine and all the surface till sheets to the east (fig. 3). It is underlain at almost all localities by the Lenzie silt and is overlain by younger lake deposits and alluvium. Thicknesses range from a few feet to over 100 feet.

The till is dark gray in color where unoxidized, buff where oxidized, clayey to silty, calcareous, massive, and jointed. It differs from the lower till, especially in sections where the lower till is overlain by the upper till, in being less compact and jointed and more bouldery. The depth of leaching is commonly less than 2 feet, but oxidation in measured sections ranges in depth from 4 feet to as much as 68 feet. Sand and gravel beds occur at the top and bottom and more rarely within the till sheet, but it is primarily a till unit.

Age and correlation.—Correlation of the upper till depends largely upon one's evaluation of the time interval between deposition of the till and the underlying Lenzie silt. During this interval the ice retreated at least 50 miles east or 35 miles northeast of the area and then readvanced to the position of the Lethbridge moraine. Traces of organic material in the Lenzie silt at Driftwood Bend suggest a possible amelioraton of climate during retreat. This evidence indicates a time break of considerable magnitude and suggests a possible correlation with either the Tazewell-Cary interval or a shorter interval within the Cary substage.

UPPER SILTS AND OTHER SURFICIAL DEPOSITS

The surficial deposits overlying the upper till in the eastern part of the area and the Lenzie silt in the western part were not studied in detail. As shown in figure 4 and as described in the geologic sections, they include a variety of sediments: lacustrine silts and clays, glaciofluvial sands and gravels, loess, alluvial wash, colluvium, volcanic ash, buried soils, dune sands, floodplain alluvium, and surficial soils. The lacustrine silts and clays and the loess deposits appear to be most widespread. Pebble zones commonly occur at the contact with the upper till or Lenzie silt and also are present in places between the upper lacustrine silts and overlying loess or alluvium.

Upper lacustrine silts.—The upper lacustrine silts and clays were deposited in the basins of proglacial lakes Lethbridge, Taber, and Bassano. Texturally they resemble the Lenzie silt, but in gen-

eral they are less oxidized and contain more organic material, which gives them a dark gray-brown color. Locally they are underlain by gravel. They are widespread and, by filling in depressions, have given rise to subdued ground-moraine topography and lacustrine plains. The lakes in which they were deposited, however, were probably short-lived, as shoreline features are rare and the lake plains are not fully developed.

Glaciofluvial sands and gravels.—Sand and gravel occur locally on the upland and as terrace deposits along Oldman River. They are present at localities *9*, *10*, *11*, and *17* and in the vicinity of Macleod form an extensive gravel plain about 50 feet above the Oldman River. Deposits related to both continental and mountain glaciation appear to be present.

Upper brown silts.—Silts, which clearly are younger than the upper lacustrine silts and terrace gravels and commonly are separated from them by a pebble zone, include alluvium, colluvium, and loess deposits. They have the uniform texture and columnar structure of loess. In other places they are horizontally stratified and sandy or pebbly, indicating an alluvial or colluvial origin (pl. 3, *B*). In most sections they are calcareous. At locality *15* a possible buried soil occurs as a 1-foot humus zone, 3½ feet below the surface.

Volcanic ash.—At locality *6* (fig. 3) a 4-inch layer of purplish-white volcanic ash occurs 6 feet below the surface within a 26-foot section of the upper brown silt (pl. 3, *B*). Mechanical analysis indicates that it is an eolian deposit (fig. 5).

The deposit is composed largely of volcanic glass shards having an index of refraction of 1.507 ± 0.002. Below $\frac{1}{16}$ mm. the material is almost 100 per cent volcanic glass. Above $\frac{1}{16}$ mm. there are abundant mineral grains of quartz, feldspar, hornblende, other heavy minerals, and unidentified coated grains. Most of the grains are angular, but grains with marked crystal outlines are present also. The heavy-mineral occurrences are summarized in table 5.

Although the ash was noted at only one locality, it is significant as a possible datum in correlating postglacial deposits. The indices suggest that it was derived from volcanics having an acid composition (George, 1924, p. 365). Some contamination is shown by the variety of heavy minerals. A postglacial volcanic ash in southwestern Glacier National Park may or may not be equivalent. This ash, which is probably from Glacier Peak in north-central Washington, has been dated in pollen studies as belonging to the postglacial xerothermic period (Hansen, 1948).

PEBBLE COUNTS

Counts were made of pebbles from all stratigraphic units except the upper silts, with the results shown in figure 6. One hundred pebbles, ½–2 inches in diameter, were counted at each locality. The variations in composition shown by the counts point to the following major conclusions:

1. The upper till differs from the lower till in having higher percentages of crystalline rocks and light-colored cherts and in having lower percentages of local Cretaceous rocks and dark-colored limestones.

2. The pebbles in the Lenzie silt show a relative concentration of quartzite and crystalline rocks as compared with the lower till from which they were derived.

3. The lower till differs from the basal till in having higher percentages of Cretaceous rocks and limestone and lower percentages of chert and quartzite.

4. The basal till in the Lethbridge section, with its high content of rounded

siliceous pebbles and low content of local Cretaceous bedrock, reflects the composition of the underlying Saskatchewan gravels.

The major compositional variation revealed by the counts is between the upper and lower tills. It indicates that much of the local bedrock had been covered by the lower till and Lenzie silt prior to the last glaciation and that, when the ice which deposited the upper till advanced into the area, it carried a high percentage of foreign material. It suggests that the lower till has a wide distribution in subsurface east of the area. From a more general point of view it opposes the notion, so commonly held, that most tills are of local derivation.

The counts were made mainly to confirm field evidence that the lower till becomes the surface till west of the Lethbridge moraine and that the overlap proposed by previous writers does not exist. Indirectly it also supports the central thesis of the paper: that the Lenzie ("interglacial") silts are proglacial lake deposits of Wisconsin age.

TABLE 5

HEAVY MINERALS IN THE VOLCANIC ASH*

Abundance	Mineral	Description
Most abundant . . (about 30–35 per cent)	Brown hornblende	Pleochroic from dark to light brown or from light brown to almost colorless; colors not deep enough for basaltic hornblende; extinction angle, 6°–15°; elongate cleavage fragments with no evidence of rounding
Abundant	Common hornblende	Greenish-brown and brownish-green; angular cleavage fragments
Common	Hypersthene-enstatite	Corroded terminations
Present	Blue-green hornblende	
	Zircon	Commonly as euhedra
	Apatite	As white rounded grains
	Diopside	With some rounded grains
	Augite	
Rare	Basaltic hornblende	
	Titanite	
	Garnet	
	Epidote	
	Spodumene (?)	
	Staurolite	

* Identified by John Bokman.

PEBBLE ZONES

The common occurrence of pebble zones ("bands") in the Alberta drift sections compared with drift sections in the Mississippi Valley region is a striking feature which merits special comment. The pebble zones occur at the lower boundaries of the basal till, lower till, Lenzie silt, and upper till and within the upper silts (figs. 4, 7; pl. 1, *B*). The pebbles are unweathered, of varied composition, unrounded, range in size from less than 1 inch to over 12 inches, and commonly form a discontinuous layer one pebble in thickness. They occur at the same stratigraphic positions in differ

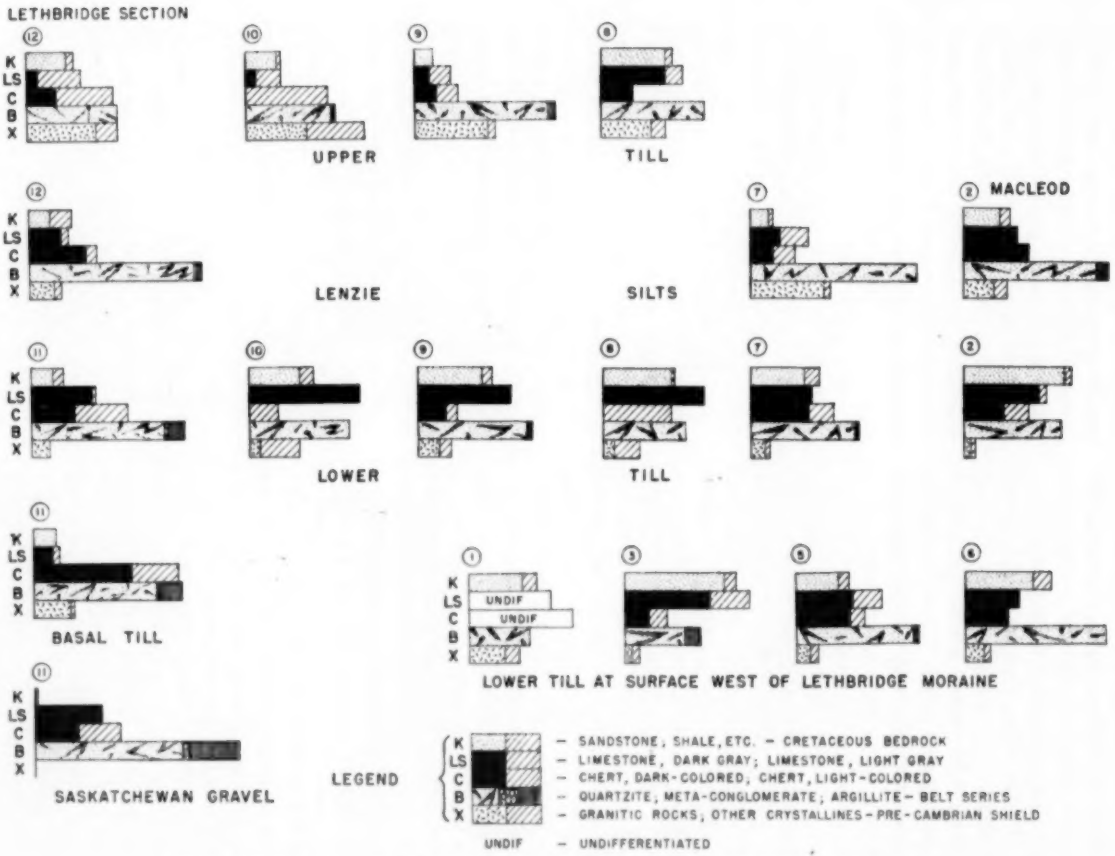

LETHBRIDGE SECTION
UPPER TILL
LENZIE SILTS
MACLEOD
LOWER TILL
BASAL TILL
LOWER TILL AT SURFACE WEST OF LETHBRIDGE MORAINE
SASKATCHEWAN GRAVEL
LEGEND
K – SANDSTONE, SHALE, ETC. – CRETACEOUS BEDROCK
LS – LIMESTONE, DARK GRAY; LIMESTONE, LIGHT GRAY
C – CHERT, DARK-COLORED; CHERT, LIGHT-COLORED
B – QUARTZITE; META-CONGLOMERATE; ARGILLITE – BELT SERIES
X – GRANITIC ROCKS; OTHER CRYSTALLINES – PRE-CAMBRIAN SHIELD
UNDIF – UNDIFFERENTIATED

FIG. 6.—Pebble composition of Pleistocene deposits. Numbers refer to locations shown in fig. 2

ent sections and in places are replaced or overlain by beds of sand or gravel. The contacts along which they occur are essentially horizontal or slope gently. None of the pebbles appear to be wind-abraded.

The pebble zones are comparable to the well-known pebble "band" at the top of the Iowan till, except for the apparent absence of ventifacts (Wilson, 1946), and can be regarded as a type of "erosion pavement" (Shaw, 1929). As such they record accelerated erosion (Lowdermilk and Sundling, 1950) and are believed to be produced by sheet- and rill-wash on surfaces unprotected or poorly protected by a vegetative cover. Their common occurrence in Alberta, as compared with

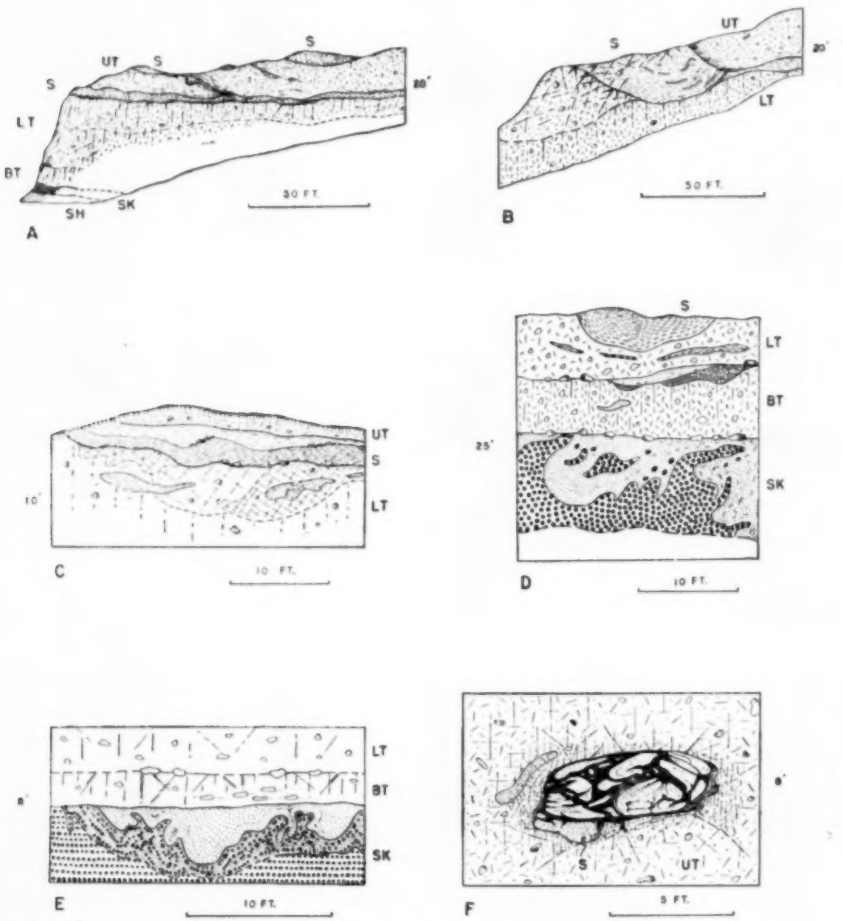


FIG. 7.—Structures produced by glacial action: *A*, locality 14 (fig. 2 and appendix); *B*, *C*, and *D*, locality 15; *E* and *F*, locality 11. *UT*, upper till; S, Lenzie silt; *LT*, lower till; *BT*, basal till; *SK*, Saskatchewan sand and gravel, disturbed and undisturbed; and *SH*, Cretaceous shale.

the Mississippi Valley, may be due to differences in climate and suggests that a drier and more rigorous periglacial environment in Alberta retarded vegetation to the extent that large areas were subjected to erosion by unconcentrated wash.

STRUCTURES PRODUCED BY GLACIAL ACTION

Deformation by overriding ice is shown in many sections by structures in the Lenzie silt and, less commonly, in the Saskatchewan gravels. The structures include: (1) upthrust masses of silt in the upper till; (2) masses of silt thrust downward into the lower till; and (3) contortions in the upper part of the Saskatchewan gravel and associated sand (fig. 7).

The upthrust masses of Lenzie silt in the upper till vary from a few inches to 50 feet in maximum diameter, and some occur in the upper till as much as 25 feet above their normal stratigraphic position. Thrust planes within the till are shown in places by the outlines of the silt masses and fractures in the till, but in other places the relations are obscure (fig. 7, *A*). At most localities the silt deposit below the inclusions, although crumpled, is continuous in its normal stratigraphic position, but in places, as shown in figure 7, *B*, it is sheared away completely. The thrust masses themselves are folded, crumpled, and fractured. Intense fracturing is shown in a few places by rounded masses of cataclastic breccia within the upper till. The breccia consists of deformed silt fragments, some of them rounded by rotation, in a matrix of comminuted silt and clay particles (fig. 7, *F*).

The second type of structure, in which lenticular masses of silt occur in the upper portion of the lower till, was noted at only one locality. It is unusual because of the apparent continuity of the silt deposit above and the association with a well-defined fracture zone in the underlying till (fig. 7, *C*).

The contortions within the Saskatchewan gravel and sand occur below the basal till and are of festoon type (fig. 7, *D*, *E;* pl. 1, *B*). They appear to involve only the upper few feet of the deposit and at most localities are completely absent. It is to be noted that the structures are truncated along the contact with the basal till, indicating that they were once more extensive and that a pebble zone occurs along the contact.

Structures due to ice-thrusting are described in numerous American and European publications (see Slater, 1925, 1926, 1927*b;* Woldstedt, 1928; Richter, 1929). In Alberta deformation of the Cretaceous bedrock by overriding ice has been described by Hopkins (1923), Slater (1927*a*), and Erdtman and Lewis (1931).

The most detailed studies are those by Slater, who recognizes two general types: (1) a crumpling and displacement of underlying deposits by ice-shove and drag, and (2) a "relict" structure inherited from debris-laden layers in the basal part of glacial ice and preserved by slow wastage.

The upthrust masses of silt in the upper till are similar to structures that have been placed in the second category by Slater. The structures are of imbricate type and are comparable to thrust planes and upthrust masses of debris at the fronts of existing glaciers (Chamberlin, 1895; Slater, 1925). However, it is difficult to explain how these features are so perfectly preserved. Even under most favorable conditions of down-wastage, differential melting and compaction must have resulted in the disturbance of englacial structures. Yet the fractures and shear zones in the till and fault contacts between the till and masses of silt are not

disrupted and deformed. Although till fabric inherited from glacier ice is known to exist at many places, it is unlikely that its preservation would require such delicate conditions of down-wastage. The thickness of upper till below silt masses, which in places amounts to 25 feet or more, also presents difficulties in terms of required ice thicknesses, but these are less critical.

In view of these difficulties it is proposed as an alternative that the imbricate structures resulted from ice-thrust during the closing stages of the glaciation recorded by the upper till. A slight readvance accompanied by accelerated movement of the ice, occurring after deposition of the lower part of the till, would probably satisfy requirements. Some of the most striking structures of this type occur at sections *14* and *15* (fig. 3), just in front of a discontinuous Lethbridge recessional moraine unit, and at section *16*, just in front of the "Chin" moraine.

The masses of silt in the lower till also are regarded as ice-thrust structures, but they probably were formed at an earlier stage of glaciation. They indicate that the lower till was solidly frozen and was fractured by ice-shove as the glacier advanced. This allowed thawed portions of the overlying silts to be squeezed downward and to flow into openings in the fractured till.

The festoon-like structures in the Saskatchewan gravels, if due to glaciation, are ice-thrust features rather than relict structures from glacier ice. However, they lack the pronounced overturned folds and thrust faults, commonly associated with such phenomena, which indicate application of a directional stress. They possess, instead, festoons and involutions which resemble frozen-ground structures developed by frost heave and thrust. It seems preferable for this reason to interpret them as structures developed in the periglacial zone and later overridden and truncated by the ice. The truncation of the structures and the existence of the pebble zone indicate, by either hypothesis, that erosion preceded the deposition of the upper till.

The imbricate structure, the fracture zones in the lower till, and the cataclastic breccia indicate that the deformed materials were frozen at the time of ice-thrusting. Local thawing to a plastic condition, however, is suggested by the lenticular masses of silt in the lower till. Flowage also is shown by structures in the Saskatchewan gravels, although these probably formed in the periglacial area rather than under the ice.

CORRELATIONS AND REGIONAL IMPLICATIONS

The Pleistocene sections in the Lethbridge area support the following major conclusions: (1) there are three recognizable till sheets, all of which appear to be of Wisconsin age; (2) the "interglacial" beds of previous writers are glacio-lacustrine deposits associated with the lower till; (3) the lower and upper tills are distinguishable on the basis of pebble composition and other physical properties; (4) a major retreat of the ice occurred prior to the deposition of the upper till; and (5) the Saskatchewan gravels are probably nonglacial in origin and cannot be used as evidence of an "Albertan" stage of glaciation.

Because there are two well-defined discontinuities in the drift section, at the base of the lower till and at the base of the upper till, it may be suggested that they represent, respectively, the Iowan-Tazewell and the Tazewell-Cary intraglacial intervals. This idea is strengthened by the fact that, although there are at least six moraines between the eastern

border of the area and the outer Wisconsin boundary, only two important breaks occur in the exposed sections.

The local evidence is partly supported by drift relations in adjoining areas. In northern Montana near Saco (fig. 1, *S*) the moraine pattern indicates an important overlap of a moraine of possible Lethbridge age across diverging older moraines, also of Tazewell or Cary age. Alden (1932, pp. 112–114), however, does not interpret this as a significant readvance. Also it is uncertain from existing maps whether the overlapping moraine is equivalent to the Lethbridge.

Another line of evidence is provided by a series of exposures in southern Saskatchewan (Johnston and Wickenden, 1931, p. 38; Wickenden, 1931) in which there are two deposits of stratified silt and sand containing plant material which separate three till sheets just outside the Altamont (outer Mankato?) moraine. The lowermost till is decomposed to a depth of 8 feet and is correlated with the Kansan, whereas the overlying tills are considered "early Wisconsin" (Iowan) and "late Wisconsin." The weathered zone and lower stratified deposits are believed to represent the Yarmouth-Illinoian-Sangamon interval, and the upper stratified deposits an interval within the Wisconsin. It is possible that the upper stratified deposits are correlative with the Lenzie silt. In this case the Lethbridge readvance would involve a distance of at least 225 miles instead of 35–50 miles and would assume a regional significance proportional to the Tazewell-Cary interval.

However, the pronounced youthful aspect of the moraines representing the lower till to the southeast and the fact that they are younger than youthful mountain-valley moraines[3] strongly suggest a Cary age. By this interpretation the readvance of the ice to the position of the Lethbridge moraine would fall within the Cary substage.

The correlation of the three tills in the Lethbridge region with Mississippi Valley substages will remain uncertain until much more information on the drift sheets of the western plains becomes available.

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[3] Unpublished studies by the writer, 1950 and 1951.

APPENDIX

Pleistocene Sections*

Section 1.—Road cut in lower till, Porcupine Hills. SE. corner of NW. ¼, Sec. 8, T. 9 N., 28 W.

Section 2.—North bluff of Oldman River, 1 mile north of Macleod. Center of SW. ¼, Sec. 24, T. 9 N., 26 W.

Section 3.—East bluff of Oldman River, 2 miles northeast of Macleod. Center N. ½, Sec. 20, T. 9 N., 25 W.

Section 4.—North bluff of Oldman River, 5 miles northeast of Macleod. SW. corner, Sec. 32, T. 9 N., 25 W. (cf. Alden, 1932, p. 74).

Deposits	Thickness (Feet)	Depth (Feet)	Deposits	Thickness (Feet)	Depth (Feet)
Recent:			*Lower till:*		
Soil, dark gray, silty	1.5	1.5	Gravel, 1–2 inches in diameter, sand matrix, lag cobbles at base	0.5	8.0
Lenzie silt:			Till, buff-gray, calcareous, jointed	5	13
Silt, buff, columnar jointing, loesslike but with scattered pebbles	6	7.5	Till, buff-gray, calcareous, massive	20	33
			Cretaceous bedrock:		
			Shale, purple-gray	30+	63+

Section 5.—South bluff of Oldman River, 2 miles south of Monarch. Center W. ½, Sec. 31, T. 9 N., 23 W.

Deposits	Thickness (Feet)	Depth (Feet)	Deposits	Thickness (Feet)	Depth (Feet)
Postglacial:			*Lenzie silt*—Continued		
Silt, brown-gray, sandy, calcareous, earthy, ½–2-inch layers; sandy gravel at base on surface of unconformity	4	4	Sand, fine to medium, gray, calcareous; horizontal beds except for gravelly cross-beds at top	2.5	82
Lenzie silt:			Gravel, sandy, pebbles up to 5 inches, discontinuous	1	83
Sand, light gray-buff, silty, calcareous, interbedded 2–4-inch silt layers	22	26	Sand and silt, pebbly, buff, calcareous, irregular bedding with cut and fill, masses of unsorted colluvium, pebble zone at base	3	86
Sand, fine, light gray-buff, very silty, calcareous; current-ripple cross-beds show transport toward east	28	54	*Lower till:*		
Silt, buff, sandy, calcareous	2	56	Till, gray-brown, partly oxidized, calcareous to top	16	102
Sand, fine, light gray, calcareous; current-ripple cross-beds show transport toward east	14	70	Gravel, sandy, silty, gray, average 1 inch	2	104
Sand, medium to coarse	1.5	71.5	*Cretaceous bedrock:*		
Sand, fine, silty	8	79.5	Shale, red-brown, weathered	10	114
			Shale, dark gray, carbonaceous	50+	164+

* The sections are shown graphically in fig. 4, and locations are given in fig. 3.

Section 6.—East bluff of Oldman River, 5 miles southeast of Monarch. Center NW. ¼, Sec. 26, T. 9 N., 23 W.

Deposits	Thickness (Feet)	Depth (Feet)
Postglacial:		
Silt, sandy, brown, earthy, unstratified	6	6
Volcanic ash, purple-white, uniform, unstratified	0.5	6.5
Silt, as above, horizontally stratified	19.5	26
Lenzie silt:		
Silt and clay, varved, laminae ½–1 inch, gray to black, calcareous	6	32
Silt, megavarves, gray-buff, calcareous, layers 1–8 inches, separated by partings of papery black clay, scattered pebbles	8	40
Colluvium, silty, pebbly, contorted; some pebbles are striated	10	50
Sand and silt, buff, calcareous, irregular 1-inch beds	15	65
Sand, gray, calcareous, poorly bedded; some silt layers	16	81
Sand and silt, varvelike, ¼–2-inch layers, buff, calcareous, current-ripple marks	8	89
Sand, gray, calcareous, poorly bedded	5	94
Silt, sandy, varvelike, ½–2-inch layers, light brown, calcareous	14	108
Colluvium, unsorted silty to bouldery debris, buff, calcareous	27	135
Lower till:		
Sand and gravel, brown, limonitic, pebbles up to 2 inches. Abundant lignite fragments	4	139
Till, dark gray, clayey with scattered pebbles, contorted sand and silt stringers, calcareous and unoxidized to top; continues below river level	78	217

Section 7.—East bluff of Oldman River, 5 miles southwest of Lethbridge. Center NE. ¼, Sec. 20, T. 8 N., 22 W.

Section 8.—East bluff of St. Mary River, 7 miles south-southwest of Lethbridge. Center W. ½, Sec. 35, T. 7 N., 22 W.

Section 9.—North bluff of Oldman River, 3 miles south of Lethbridge. SW. corner of NW. ¼, Sec. 18, T. 9 N., 21 W.

Section 10.—East bluff of Oldman River, 3 miles south of Lethbridge. NE. ¼ of SW. ¼, Sec. 17, T. 8 N., 21 W.

Deposits	Thickness (Feet)	Depth (Feet)
Postglacial:		
Silt, gray, loesslike	4	4
Upper till (Lethbridge moraine):		
Gravel, sandy, average 2 inches	10	14
Till, gray-brown, calcareous	20	34
Lenzie silt:		
Sand, silty, gray, calcareous, cross-bedded; some varvelike layers with graded bedding	9	43
Silt, sandy, buff, calcareous, ripple-mark cross-bedding in layers 2–4 inches thick; sand and clay layers; subaqueous-type slump structures	11	54
Silt, buff, calcareous; indistinct beds, 1–1½ inches thick, show on wind-etched surfaces (pl. 2, *B*)	4	58
Sand, fine, silty, grayish-tan, calcareous; inclined beds dip west; silt with black-clay partings occurs at top	0.8	58.8
Silt, varves ¼ inch thick, buff, calcareous	4.2	63
Silt, megavarves with graded bedding and papery black-clay partings at top, buff, calcareous; thicknesses of units, from top to bottom, are: 16, 10, 20, 22, 16, 15, 12, 5.5, 10, 11, 4.5, 4, 6.5, 7, 3.5, and 3 inches	12	75
Silt, buff, calcareous, poorly stratified, scattered pebbles	3	78
Lower till:		
Till, brown-gray, calcareous	36	114
Cretaceous bedrock:		
Shale, sandy, light gray	50+	164+

Section 11.—Exposures along Highway 3 at west edge of Lethbridge. SE. ¼, Sec. 1, T. 9 N., 22 W.
Section 12.—Type section of Lenzie silt. West bluff of Oldman River, ½ mile north of highway bridge at Lethbridge. SW. ¼ of SE. ¼, Sec. 11, T. 9 N., 22 W. (cf. Dawson and McConnell, 1895, p. 40; Alden, 1932, pp. 71–74).

Deposits	Thickness (Feet)	Depth (Feet)
Upper till (Lethbridge moraine):		
Till, gray-brown, calcareous, lower 20 feet unoxidized; rude layering and silt inclusions in lower part; local sand and gravel at base	40	40
Lenzie silt:		
Silt, megavarves with graded beds 3–18 inches thick and papery black-clay partings, buff, calcareous	8	48
Silt, tan, calcareous; indistinct horizontal beds; some sand layers; scattered pebbles	4	52
Silt and sand, tan to gray, calcareous, cut-and-fill channels; possible eolian cross-bedding in 3-foot bed at top	32	84
Silt, buff, calcareous, rudely stratified; some pebbles and clay layers	11	95
Clay, black, stratified; composed of Cretaceous lignite and black-shale particles; discontinuous	3	98
Lenzie silt—Continued		
Sand, gray-tan, calcareous, current bedding	5	103
Lower till:		
Till, dark gray, upper 20 feet oxidized brown-gray, calcareous, compact; pebble zone at top; sand at base	36	139
Basal till:		
Till, dark gray, calcareous, compact, columnar jointing	5	144
Saskatchewan gravels:		
Gravel, dominantly quartzite and chert, average about 2 inches, well rounded, gray-sand matrix, partly oxidized, rude horizontal bedding	15	159
Cretaceous bedrock:		
Shale, black, carbonaceous	20	179

Section 13.—West bluff of Oldman River, 4 miles north of Lethbridge. Center N. ½, Sec. 24, T. 9 N., 22 W.

Section 14.—East bluff of Oldman River, 4½ miles north of Lethbridge. Center E. line, Sec. 30, T. 9 N., 21 W.

Section 15.—Deep gully developed along drainage ditch, 6 miles north of Lethbridge on east side of Oldman River. Center SW. ¼, Sec. 4, T. 10 N., 21 W.

Deposits	Thickness (Feet)	Depth (Feet)
Postglacial:		
Soil, dark brown	1.5	1.5
Loess, buff, calcareous, caliche veinlets	2	3.5
Soil, gray-black, calcareous	1	4.5
Loess, buff, calcareous; pebble zone at base	1.5	6
Lake Lethbridge silt:		
Silt, varved, and sand, brown-gray, calcareous; pebble zone at base	4	10
Upper till (Lethbridge ground moraine):		
Till, buff, oxidized, calcareous	10	20
Till, dark gray, calcareous, oxidized joints	50	70
Lenzie silt:		
Silt, buff, and sand, gray, calcareous, stratified; includes some colluvium; deformed and discontinuous as a result of ice-thrust	8	78
Lower till:		
Till, clayey, dark gray, calcareous, upper 6 feet oxidized brown, dense, columnar, oxidized joints, scattered pebbles; pebble zone at base	20	98
Gravel and silty sand, discontinuous	3	101
Basal till:		
Till, clayey, dark gray, calcareous, very compact, columnar; pebble zone at base	10	113
Saskatchewan gravels:		
Sand, silty, gray; similar to matrix in underlying gravel; discontinuous	2	115
Gravel, largely quartzite and chert, average about 2 inches, maximum 6 inches, well-rounded, gray-sand matrix, sand lenses; upper 6 feet contorted; horizontal and foreset bedding; foresets at one point dip south	14	129
Cretaceous bedrock:		
Shale, weathered rust; upper few feet earthy and limonitic; undulatory upper surface	10	139
Shale, dark gray, some thin sandstone and limestone layers	15+	154+

Section 16.—Deep gully on north side of Oldman River, 15 miles northeast of Lethbridge near Coaldale Bridge. SE. ¼ of NE. ¼, Sec. 35, T. 10 N., 20 W.

Deposits	Thickness (Feet)	Depth (Feet)
Lake Lethbridge silt:		
Silt, sandy, brown, calcareous, stratified; fills depression on underlying till sheet; locally reworked by wind and slope wash	15	15
Upper till (Lethbridge ground moraine):		
Till, dark gray, calcareous; silt, sand, and gravel lenses	45	60
Lenzie silt:		
Silt, buff, and sand, gray, stratified, scattered pebbles; deformed and discontinuous as a result of icethrust	10	70
Lower till:		
Till, clayey, dark gray, calcareous, compact, columnar, oxidized joints, scattered pebbles and boulders; sand and gravel at base	102	172
Basal till:		
Till, clayey, dark gray, calcareous, very dense	8	180
Saskatchewan gravels:		
Gravel, largely quartzite and chert, average 2 inches, maximum 8 inches, well rounded, matrix and some layers of gray silty sand; 6-inch iron-stained zone at top	8	188
Cretaceous bedrock:		
Shale, weathered rust, earthy	6	194
Shale, dark gray	8	202
Shale, gray, with sandstone; to river level	16	218

Section 17.—North bluff of Oldman River at Driftwood Bend, 13 miles north of Taber. Center Sec. 4, T. 12 N., 16 W. (cf. Dawson, 1885, pp. 6, 15; Dawson and McConnell, 1895, p. 40; Johnston and Wickenden, 1931, pp. 32–33).

Deposits	Thickness (Feet)	Depth (Feet)
Upper till:		
Till, gray, calcareous, sand layers; inclusions of Cretaceous black shale and clay ironstone concretions	60	60
Lenzie silt:		
Silt and fine sand, light gray, calcareous, stratified with some cross-bedding	8	68
Colluvium, sandy clay with pebbles, buff, slightly calcareous; fragments of small shells, some identifiable as pelecypods; discontinuous	4	72
Sand, yellow-brown, discontinuous	3	75
Lower till:		
Till, clayey, dark gray, calcareous, unweathered, dense, jointed; 4-foot oxidized zone at top; oxidized gravel parting at base	37	112
Basal till:		
Till, clayey, brown-gray, calcareous, unweathered, dense, jointed, sand lenses	4	116
Sand, coarse, gray, stratified, discontinuous	5	121
Saskatchewan gravels:		
Gravel, largely quartzite, average 2 inches, well rounded, sand matrix; contact with underlying Cretaceous shale covered	2+	123

Section 18.—North bluff of Oldman River at Wolf Island, 7 miles north of Purple Springs. S. ½ of NW. ¼, Sec. 20, T. 11 N., 14 W. (cf. Dawson, 1885, pp. 3, 15; Dawson and McConnell, 1895, p. 40; Johnston and Wickenden, 1931, pp. 33–34). Section badly slumped.

Deposits	Thickness (Feet)	Depth (Feet)	Deposits	Thickness (Feet)	Depth (Feet)
Upper till:			*Lenzie silt*—Continued		
Till, gray-brown, calcareous, exposed at crest of bluff	5	5	cles, ripple-mark cross-bedding, partly oxidized	5	17
Lenzie silt:			*Lower till:*		
Silt and clay, varved, buff, calcareous	6	11	Till, clayey, dark gray, calcareous, unweathered; lower contact covered	12+	29+
Clay, varved, dark gray	1	12			
Sand, gray, abundant dark minerals and shale and lignite parti-					

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CHEMICAL BONDS AND DISTRIBUTION OF CATIONS IN SILICATES[1]

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ABSTRACT

It is shown on theoretical grounds that the electronegativity of oxygen in silicates depends upon the Si-O structure as well as upon the Al/Si ratio in the $(Si/Al)O_4$ tetrahedra. The more Si-O-Si links in a silicate structure, the larger the electronegativity of the oxygen atoms attached to metallic ions. That is, the effective electronegativity value of oxygen increases stepwise through the sequence: orthosilicate → pyrosilicate $(Si_2O_7^{6-})$ → metasilicate (SiO_3^{2-}) → double-chain silicate $(Si_4O_{11}^{6-})$ → phyllosilicate $(Si_2O_5^{2-})$ → tectosilicate. This means that the corresponding hypothetical acids increase in strength through the sequence and that the metal-oxygen bonds in the corresponding salts become more *ionic* throughout the series. It is demonstrated that the "base exchange" of cations between two oxysalts commonly takes place in such a way that the most electropositive metal combines with the most acidic anion, and the less electropositive metal with the less acidic anion. This combination generally represents the lowest total energy and the highest bond energy. It is shown how the different metallic cations distribute themselves among the different types of silicates, depending on the variable electronegativity of oxygen in the structures and on the position of the metals in the electronegativity scale of elements. The rock-making minerals are in good agreement with the theory.

DISTRIBUTION OF Fe AND Mg AMONG SILICATES

Although V. M. Goldschmidt and others have explained the general rules governing the distribution of elements in minerals, the subject is still far from understood. It is customary to regard the silicates and metallic oxides in the lithosphere as strictly ionic compounds and hence to give major weight to size of ions and their electrical charges in the explanation of the element distribution among these minerals.

It is well known, however, that it is chiefly the character of the valency forces which causes some elements to be chalcophile, others to be siderophile, and still a third group to be lithophile (Goldschmidt, 1937). The properties of Zn, for example, have been discussed from this viewpoint by H. Neumann (1949).

It also seems to be the case that among the lithophile elements there are differences in bond type, less pronounced than those between the major groups, which cause some elements to build certain types of silicates, other elements to build different silicates. That this is true will be shown on the following pages.

As most cations are of different sizes, it is often difficult, if not impossible, to decide whether a given element distribution among minerals is due to the difference in ionic sizes (or ionic charge) or to dissimilarities in valency forces, as, for example, differences in the degree of covalency of the bonds.

In some cases, fortunately, two (or more) ions are closely similar in size and have the same charge, such as Mg^{2+} and Fe^{2+}. If such ions show diverging tendencies to build minerals, it may be due to some qualitative bond differences not explainable by the classic ionic theory. The ions Fe^{2+} and Mg^{2+} do not behave as one would expect on the basis of their similar radii, 0.83 and 0.78 Å, respectively. These two ions are unevenly distributed among silicates. Cordierite, for example, commonly has much more Mg than Fe, garnet prefers Fe, talc has almost solely Mg, and staurolite takes only Fe.

In this paper the influence of bond character on the geochemical distribution

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of elements among silicates will be discussed. To this end the Fe-Mg distribution is a convenient starting point, and some simple ferromagnesian silicates in which the Fe-Mg distribution is partly known can be examined. The following group of minerals comprise the most common types of Si-O structures (the tectosilicates do not form ferromagnesian compounds):

Olivine: $(Mg,Fe)_2SiO_4$ = orthosilicate,
Pyroxene: $(Mg,Fe)SiO_3$ = single-chain metasilicate (inosilicate),
Anthophyllite: $(Mg,Fe)_7Si_8O_{22}(OH)_2$ = double-chain silicate (inosilicate),
Talc: $(Mg,Fe)_3Si_4O_{10}(OH)_2$ = sheet-type silicate (phyllosilicate).

The distribution of Fe and Mg in coexisting olivine and pyroxene has been studied in some detail by the writer and DeVore (1951). Figure 1 clearly demonstrates that Fe is enriched in olivine, Mg in pyroxene.

Bowen and Schairer (1935) have some data from synthetic pyroxene and cummingtonite[2] (table 1). The Fe-Mg distribution hardly represents equilibrium, but there is no doubt that the trend of the partition is correct, cummingtonite preferably taking magnesium, pyroxene preferring iron. No detailed study has been made of the Fe-Mg distribution in talc and anthophyllite, but this case is so obvious that no such detailed information is needed for our present purposes. Talc is almost a pure magnesium silicate, whereas it is well known from a few analyses that anthophyllite is commonly rather rich in iron. (Minnesotaite was shown by Gruner in 1944 to be an iron-rich talc analogue. He states that this iron-talc exhibits many signs of unstable structure; actually, the very rarity of it is a manifestation of the difficulty with which iron replaces magnesium in a silicate structure of the talc type.) It is safe, therefore, to conclude that, if talc and anthophyllite coexist in equilibrium, the former will be the more magnesium-rich mineral of the two. It is thus demonstrated that, provided that equilibrium exists among the minerals, the Mg/Fe ratio will increase in the series: olivine → rhombic pyroxene → hornblende (anthophyllite) → talc.[3] The petrologist may note that this distribution is opposite to the change in Fe/Mg ratio that occurs during cooling and solidification of a magma, in which the early olivines are rich in magnesium, the late hornblendes rich in iron. This last sequence, however, is formed under typical nonequilibrium conditions and is hence irrelevant to our present problem. See also the discussion of the influence which Al in the Si position has on the Fe-Mg distribution (p. 345).

TABLE 1

Fe-Mg Distribution in Pyroxene and Cummingtonite: $Mg/(Mg + Fe)$*

Pyroxene	Cummingtonite
1.00	1.00
0.84	0.87
0.68	0.73
0.47	0.62
0.26	0.48
0.00	0.00

* Data after Bowen and Schairer (1935).

[2] The structure of anthophyllite and cummingtonite are almost identical.

[3] Actually, we could also place a silicate melt at the head of this sequence, as demonstrated by high-temperature syntheses, the melt tending to have a greater Fe/Mg ratio than the minerals in equilibrium with it.

It is apparent now that the Fe-Mg distribution is closely related to the type of Si-O framework of the minerals, the nesosilicate being richer in iron than the single-chain inosilicate, this latter being richer in iron than the double-chain inosilicate, which, in turn, is more iron-rich than the phyllosilicate. Unfortunately, there exists no common tectosilicate of iron and/or magnesium, so we have no example of Fe and Mg behavior in this structural type. In our selected mineral group we have considered only silicates that contain the same chemical elements, namely, Mg, Fe, Si, and O (and some H), and that differ chiefly in their Si-O framework. The reason for the observed Fe-Mg partition should, therefore, be first sought in the different Si-O frameworks. In order for different Si-O structures to discriminate between Mg and Fe, the two ions must be unlike in some significant respect. Although they are closely similar in size, they are dissimilar in other ways. In particular, their electronegativity values, which are very significant as indicators of chemical affinity and bond types, are rather different. According to Pauling and Haissinsky (see table 2), the values are $X_{Mg} = 1.2$ e.v. and $X_{Fe} = 1.6$ e.v. Possibly the diverging character of the valency forces of Mg and Fe, as indicated by their different electronegativity values, is the

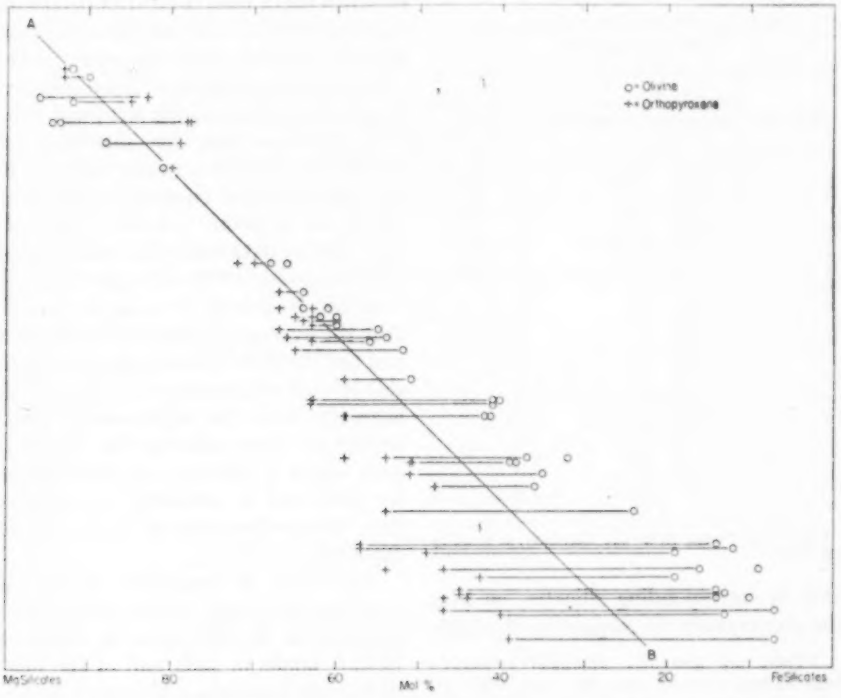


FIG. 1.—Mg/(Mg,Fe) ratios in coexisting pairs of olivine and pyroxene (Ramberg and DeVore, 1951)

major reason for their uneven distribution among the several silicates. We shall test this assumption.[4]

The observed Fe-Mg partition among the silicates may be illustrated by the simplified equations (1), (2), and (3).

The actual situation is complicated by the fact that Fe and Mg are exchangeable in corresponding silicates, so that the mix crystals $(Fe,Mg)_2SiO_4$, $(Fe,Mg)SiO_3$, $(Fe,Mg)_7Si_8O_{22}(OH)_2$, and $(Mg,Fe)_3Si_4O_{10}(OH)_2$ will appear in the equations. However, the observed Fe-Mg distribution shows that all three equations are displaced to the right-hand side, at the common pressure-temperature conditions occurring during rock formation. If we therefore assume, as is reasonable in our case, that the bond energies of the minerals carry more weight in determining their stability than do their entropies, we can conclude that the sums of the bond energies on the right-hand sides are larger than those on the left-hand sides and therefore that the reactions are exothermic. This is actually shown to be the case in the first equation, which has a ΔH equal to about $-2{,}310 \pm 490$ cal., according to data available from Sahama and Torgeson (1949). Our problem will therefore be solved if it can be proved that the average strength of the Fe-O-Si and the Mg-O-Si bonds on the right-hand side of each of equations (1), (2), and (3) is greater than that of the similar bonds on the left-hand side. As the details of such bonds in silicates are little known, we shall find it advisable to consider, first, similar bonds in the better-known oxysalts.

TABLE 2

ELECTRONEGATIVITY VALUES OF SOME ELEMENTS*

Element	Electronegativity (e.v.)	Element	Electronegativity (e.v.)
Li	1.0	O	3.5
Na	0.9	S	2.5
K	0.8	F	4.0
Rb	0.8	Cl	3.0
Cs	0.7	Br	2.8
Be	1.5	I	2.6
Mg	1.2		
Ca	1.0		
Sr	1.0		
Ba	0.85		
B	2.0		
Al	1.5		
Fe^{2+}	1.65		
Fe^{3+}	1.8		
C	2.5		
Si	1.8		
N	3.0		
P	2.1		

* Data after Pauling (1948) and Haissinsky, as listed by Fyfe (1951).

The heats of formation of oxysalts from the basic and acidic oxides give a measure of the difference in energy of M-O-A bonds in salts and of the mean of the bond energies, M-O and A-O, in the basic and acidic oxides (M stands for a metal, A for a metalloid). Table 3 shows the heats of formation of several oxysalts from the oxides. Figure 2 shows the same data arranged according to po-

[4] There are numerous additional indications from natural minerals that Fe^{2+} and Mg^{2+} exhibit diverging types of valency forces. For example, Fe is a very common constituent of sulfides, Mg is not. Iron may occur in 4-co-ordination in some silicates (staurolite); Mg is in 6-co-ordination in all known cases in silicates. These are strong indications of a certain covalent tendency in iron which is absent in magnesium.

$$\underset{\text{olivine}}{Mg_2SiO_4} + 2\underset{\text{pyroxene}}{FeSiO_3} \rightarrow \underset{\text{olivine}}{Fe_2SiO_4} + 2\underset{\text{pyroxene}}{MgSiO_3} + \Delta H\,, \qquad (1)$$

$$7\underset{\text{pyroxene}}{MgSiO_3} + \underset{\text{anthophyllite}}{Fe_7Si_8O_{22}(OH)_2} \rightarrow 7\underset{\text{pyroxene}}{FeSiO_3} + \underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + \Delta H_2\,, \qquad (2)$$

$$3\underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + 7\underset{\text{minnesotaite}}{Fe_3Si_4O_{10}(OH)_2} \rightarrow 3\underset{\text{anthophyllite}}{Fe_7Si_8O_{22}(OH)_2} + 7\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \Delta H_3\,. \qquad (3)$$

sition in the periodic table. The amazingly regular correlation between energy of salt formation and position of the metals in the periodic table is demonstrated in this figure. The electronegativity values, as given by Pauling and Haissinsky, are noted after each metal, and it is apparent also that the regularity remains if one considers heat of salt formation against electronegativity of metal atoms. There is also an excellent relation between the energy of salt formation and the strength

TABLE 3

HEATS OF FORMATION OF OXYSALTS FROM OXIDES*

METAL	HEATS OF FORMATION (KCAL/MOL)					
	$2M(OH)$	M_2CO_3	$2MNO_3$	M_2SO_4	$\frac{1}{3}M_3PO_4$	$\frac{1}{4}M_4P_2O_7$
Li	22.43	53.35	89.00	106.15	.....	.....
Na	36.1	75.99	124.59	137.13	85.22	98.16
K	49.47	93.81	150.58	162.56	112.7†	122.5†
Rb	51.33	96.31	156.18	167.68	.....	.....
Cs	49.93	96.21	160.70	168.85	.....	.....

METAL	HEATS OF FORMATION (KCAL/MOL)			
	$(OH)_2$	MCO_3	$M(NO_3)_2$	MSO_4
Be	3.43	.....	.....	52.1
Mg	3.23–9.43	27.45	63.11†	64.95
Ca	15.93	43.35	72.97	95.1
Sr	19.53	55.15	93.0	110.6
Ba	24.53	63.45	104.5	122.5

* Data from Bichowsky and Rossini (1936).
† From aqueous solutions.

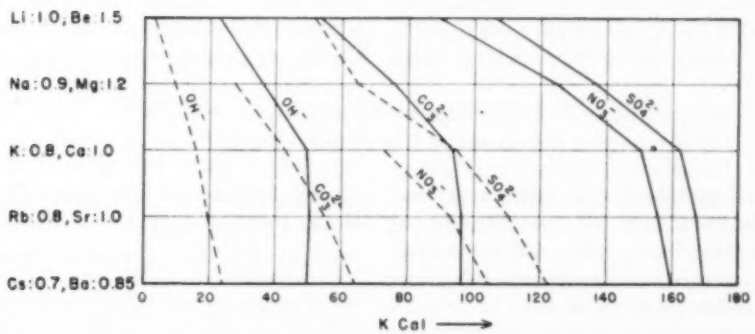


FIG. 2.—Heats of formation at room temperature of various salts from their constituent oxides. The dashed lines refer to the salts of the earth alkali metals; the solid lines refer to the salts of the alkali metals. The numbers after each metal are the electronegativity values (Pauling, 1948) of the corresponding metal.

of the acids, the strongest acids giving higher heats of salt formation with a given metallic oxide. The dissociation constants for the aqueous solutions of some of the acids are given in table 4 to show their relative strength. These data demonstrate that heat of salt formation from the oxides is highest when the oxide of an electropositive metal (low electronegativity value) combines with a strongly acidic oxide.[5] Of particular importance is the fact that the energy curves in figure 2 converge toward the left above the figure. This shows that, *in a base exchange reaction among salt pairs, the reaction will be exothermic toward the salt of the strongest acid and the most electropositive metal oxide.* Some examples show this quantitatively:

TABLE 4

DISSOCIATION CONSTANTS OF SOME OXYACIDS IN AQUEOUS SOLUTIONS*

Acid	Temperature (° C.)	Dissociation Constant for First H^+ Ion
H_3BO_3	25	6.5×10^{-10}
H_2CO_3	25	3.1×10^{-7}
HNO_3	Room	1.2×10
Al hydroxide	25	6.2×10^{-13}
H_4SiO_4	30	2.2×10^{-10}
H_3PO_4	25	7.5×10^{-3}
H_2SO_4	25	4×10^{-1}(?)
$HClO_4$		Very large

* Data from Roth and Scheel (1936).

Heats of salt formation from oxides: $\underset{106.15\text{ kcal.}}{Li_2SO_4} + \underset{96.2\text{ kcal.}}{Cs_2CO_3} \rightarrow \underset{53.3\text{ kcal.}}{Li_2CO_3} + \underset{168.9\text{ kcal.}}{Cs_2SO_4} - 19.85\text{ kcal.}$ (202.35 kcal. / 222.2 kcal.)

Heats of salt formation from oxides: $\underset{64.9\text{ kcal.}}{MgSO_4} + \underset{24.5\text{ kcal.}}{Ba(OH)_2} \rightarrow \underset{9.4\text{ kcal.}}{Mg(OH)_2} + \underset{122.5\text{ kcal.}}{BaSO_4} - 42.5\text{ kcal.}$ (89.4 kcal. / 131.9 kcal.)

Here Cs_2SO_4 and $BaSO_4$, respectively, are salts of the strongest acid and the strongest base (most electropositive metal). Both these salts are on the exothermic or low-total-energy side (high bond energy) of the equations.

We certainly cannot expect the principle discussed above to be without exceptions. One must, in particular, be careful if the base exchange takes place between salts having either acids or bases or both of closely comparable strength (see, for example, the nitrates and sulfates in fig. 2). It should also be understood that the reactions may be reversed at high temperature, because the entropy is highest for the most loosely bound salts, which therefore may be stabilized at high temperature. That the principle holds good for many ferrous and magnesian salts is demonstrated by the following reactions:

$$Mg(OH)_2 + FeCO_3 \rightarrow Fe(OH)_2 + MgCO_3 - 12.4\text{ kcal.}$$
$$MgS + FeCO_3 \rightarrow FeS + MgCO_3 - 36.1\text{ kcal.}$$

The energy data are from Bichowsky and Rossini (1936). In all cases the salts of the stronger base, MgO, and the strongest acids are on the low-energy side of the base exchange reactions.[6]

The ferromagnesian silicate reactions on page 334 can now be explained in light of the principle just demonstrated if it

[5] Incidentally, it is reasonable that the energy of salt formation from oxides is a more fundamental measure of strength of acidic or basic oxides than is their dissociation constant in aqueous solutions.

[6] It should be noted, however, that this is not true in all cases involving magnesium sulfate. This salt has a low heat of formation and commonly shifts the reaction to the wrong side: $MgSO_4 + FeCO_3 \rightarrow MgCO_3 + FeSO_4 - 11.6$ kcal. This, in connection with the fact that the point for $MgSO_4$ does not fit well in fig. 2, makes it tempting to wonder if the old measured heat of formation of $MgSO_4$ is in error.

can be shown independently that the strength of the hypothetical silicic "acids" increases in the following sequence:

$$H_4SiO_4 \rightarrow H_2SiO_3 \rightarrow H_7Si_8O_{22}(OH)_2 \rightarrow H_3Si_4O_{10}(OH)_2 .$$

(As noted above, the strength of the acids may be measured by means of the heats of formation of the corresponding silicates from the oxides.) By analogy with ordinary oxyacids, one indeed has reason to think that this is the case because pyroacids, which are characterized by A-O-A bridges like the complex silicates, really are stronger than the simple acids. Thus, for example, orthophosphoric acid, H_3PO_4, is considerably weaker than pyrophosphoric acid, $H_4P_2O_7$, as seen from table 5. It is also seen that the heats of formation of pyrophosphoric salts are greater than those of phosphoric salts (as shown in table 3).

TABLE 5

DISSOCIATION CONSTANTS OF PHOSPHORIC AND SILICIC ACIDS

Acid	Temperature (° C.)	Dissociation Constant
H_3PO_4		
For first H^+	25	7.52×10^{-3}
For second H^+	25	6.23×10^{-8}
For third H^+	20	1.2×10^{-12}
$H_4P_2O_7$		
For first H^+	18	1.4×10^{-1}
For second H^+		3.2×10^{-2}
For third H^+		1.7×10^{-6}
For fourth H^+		6.0×10^{-9}
H_4SiO_4		
For first H^+	30	2.2×10^{-10}
Colloidal silicic acid		
For first H^+	23	2.3×10^{-4}

A strong oxyacid is one in which the O-H bond is largely ionic in character; it will dissociate easily in water. In salts of strong acids, the bond M-O is also decidedly ionic: the stronger the acid, the more ionic the M-O bonds when M remains the same metallic ion. The A-O bonds in the anion change from acid to acid, and therefore the bonds from the oxygen to the metals will also change. The more covalent and double the A-O bond, the more ionic the M-O bond in the M-O-A link in salts. The more covalent and double the A-O bond, the higher the electron density between A and O because the electrons are partly displaced from A and O toward the bond between them. For that reason, the electron affinity as well as the ionization potential of the oxygen on the opposite side of the A atom will be greater than that of a less doubly bound oxygen atom, such that

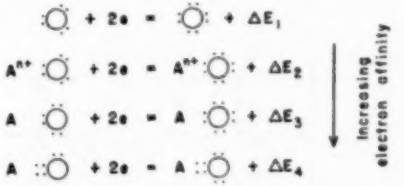
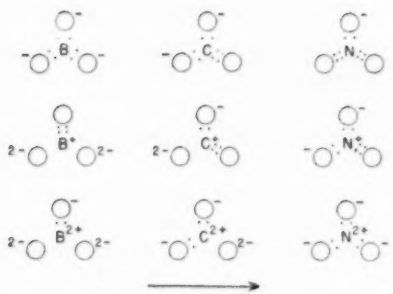


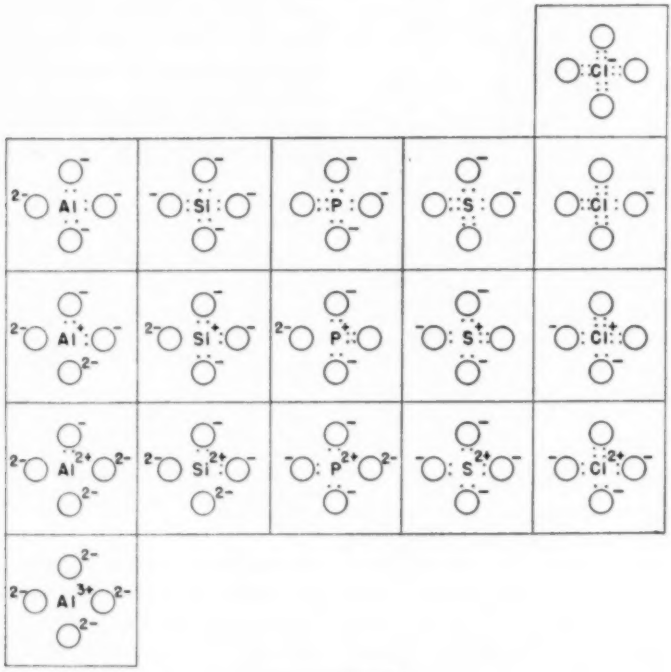
FIG. 3.—The change of electron affinity of an oxygen atom in different situations (*1*) as a free atom; (*2*) attached by electrostatic force to a positive ion, A^{2+}; (*3*) bound to A by a two-electron covalent bond; and (*4*) bound by A to a four-electron covalent bond.

the tendency of the strongly bound oxygen atom to capture an electron from metals increases and its tendency to build ionic bonds toward metals becomes more pronounced (fig. 3). This is strikingly demonstrated by the oxyacids of some first- and second-row elements. The strength of these acids increases as follows: $H_3BO_3 \rightarrow H_2CO_3 \rightarrow HNO_3$ and $H_4SiO_4 \rightarrow H_3PO_4 \rightarrow H_2SO_4 \rightarrow HClO_4$ (table 4). As indicated in figure 4, the bond A-O becomes more double in char-



A

FIG. 4.—*A*, some of the electron configurations present in the anion of the ortho-oxyacids of the first-row elements.



B

FIG. 4.—*B*, some of the possible electron configurations present in the anion of the ortho-oxyacids of the second-row elements.

acter through the sequence $BO_3^{3-} \rightarrow CO_3^{2-} \rightarrow NO_3^-$ of the first-row elements and also through the sequence $SiO_4^{4-} \rightarrow PO_4^{3-} \rightarrow SO_4^{2-} \rightarrow ClO_4^-$ of the second-row elements. The relative strengths of the above-mentioned acids are also confirmed by the heats of formation of their salts, as shown in table 3 and figure 2 as well as in table 6.

TABLE 6

HEATS OF FORMATION OF SALTS FROM OXIDES: FIRST- AND SECOND-ROW ELEMENTS*

Salt	Heat of Formation (Kcal/Gm Atom Ca)
$Ca_2(BO_3)_2$	20.9
$CaCO_3$	43.35
$Ca(NO_3)_2$	72.94
Mg_2SiO_4	7.56
$Mg_3(PO_4)_2$	39.2
$MgSO_4$	64.95
$Mg(ClO_4)_2$	Unknown

*Data from Bichowsky and Rossini (1936) and from Sahama and Torgeson (1949) (Mg_2SiO_4).

Realizing that we are at the heart of our problem, we shall in our further discussion consider the Si-O constructions in the silicates and see how the complexity of the Si-O framework affects the ionic character of the O-M bonds. Figure 5 shows schematically the Si-O constructions in the group of minerals discussed.

Starting with the orthosilicate anion (fig. 5), it is believed that the Si-O bonds are about 50 per cent covalent and 50 per cent ionic in character (Wells, 1950). That is, the electron density is considerable in the space between the Si and O atoms. Actually, the Si-O bonds in the orthosilicate anion have considerable double-bond character with four shared electrons between Si and O. This is indicated by the very short Si-O distance in silicates (Pauling, 1948). The partly covalent and double Si-O link affects the oxygen atom in such a way that its opposite side behaves as if its electronegativity has increased. In orthosilicates, therefore, the M-O bonds are chiefly ionic. Figure 6 shows some of the possible structures among which the SiO_4 ion resonates.

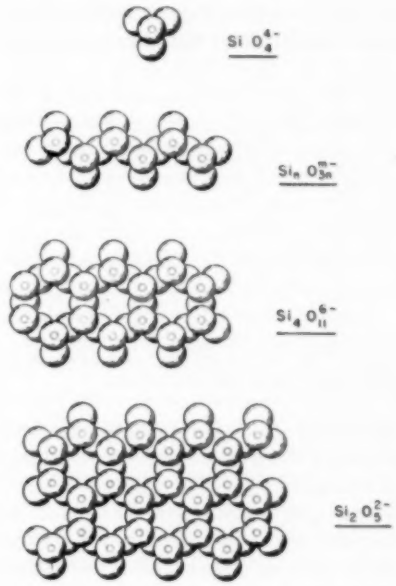


FIG. 5.—The structures of the anion in different silicates.

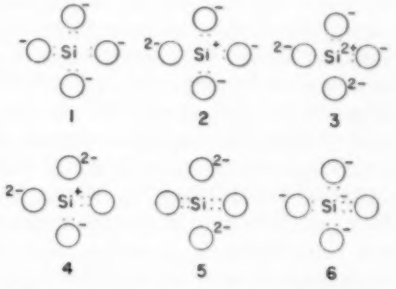


FIG. 6.—Possible electronic structures among which the orthosilicate anion resonates.

Turning from orthosilicates to metasilicates, we find that some of the M-O bonds have changed to Si-O bonds, giving rise to Si-O-Si bridges. It is most important at this point to note that the silicon atom, which replaces M in a Si-O-M link to form a pyro- or metasilicate bridge, will discriminate among the oxygen atoms in the original SiO_4 tetrahedron in such a way that the new silicon

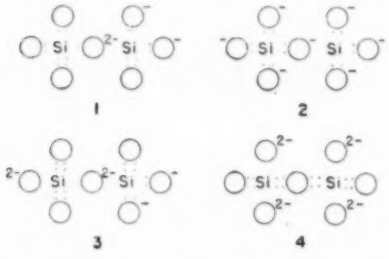


FIG. 7.—Possible electronic structures among which the pyrosilicate anion resonates.

will attach itself preferably to the ionic oxygen in the resonating SiO_4 structures. Of the several possible electronic structures among which a pyrosilicate ion can resonate, the one with ionic $Si^+O^{2-}Si^+$ linkage is therefore somewhat more stable and probable than the one with double-bond Si=O-Si linkage (see fig. 7). The reason for this conclusion is that the ionic oxygen in the SiO_4 structures (fig. 6) has the lowest electronegativity value, and doubly bound oxygen the highest. (As discussed above, we consider here the electronegativity of the outer parts of the oxygen in the SiO_4 anion.) On the other hand, Si is less electropositive than most metals represented by M in the Si-O-M link, these metals being Mg, Fe, Ca, the alkalis, etc. The most stable arrangement in a metasilicate is, therefore, that in which silicon is attached to the least electronegative ionic oxygen in the SiO_4 tetrahedra, these ionic oxygen atoms then acting as bridges between the silicon atoms. Among the possible structures of the $(Si_nO_{3n})^{-2n}$ ion, the one shown in figure 8, *2*, is somewhat more likely than that shown in figure 8, *1*, and therefore plays a more important role in the resonating structures.

For the reasons discussed above, we also find that the nonbridging oxygen atoms which surround Fe, Mg, Ca, etc., in olivine and pyroxene *have a greater percentage of double-bond character toward silicon in metasilicates than in orthosilicates*. It follows, then, that the oxygens that surround metal ions are more electronegative in metasilicates than in orthosilicates. Combining this conclusion with the principle of base exchange discussed previously, it is evident why the electropositive magnesium strives to build metasilicates, the less electropositive iron to make orthosilicates.

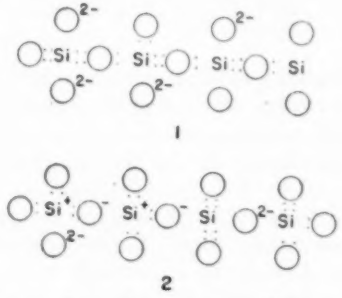


FIG. 8.—Two rather extreme possibilities of the electronic structures of metasilicate anion.

Now consider the double-chain Si-O constructions as found in anthophyllite and shown in figure 5. Here 50 per cent of the SiO_4 tetrahedra share two oxygen atoms each, as in the single-chain pyroxene structure, and 50 per cent of them share three oxygen atoms each, as in talc and other phyllosilicates. Let us call these SiO_4 tetrahedra the "pyroxene type" and the "talc type," respectively.

One would expect the valence character of the nonbridging oxygen in the pyroxene-type tetrahedra (in anthophyllite) to be practically identical to that of the pyroxene minerals treated above. But the talc-type tetrahedra contain three shared oxygen atoms, all three bonds being quite ionic in character, as we have already seen.

Three rather ionic Si-O″ bonds allow silicon to make the fourth bond to nonbridging oxygen considerably more covalent and double in character than the Si-O′ bonds in pyroxene-type tetrahedra (O″ denotes bridging oxygens; O′ denotes nonbridging). On the average, therefore, the O′-oxygen in double-chain silicates is more electronegative or has greater electron affinity than in single-chain silicates. *In conclusion, we see that anthophyllite prefers magnesium relative to pyroxene for the same reason that pyroxene prefers magnesium relative to olivine.*

It is now straightforward to consider talc because here all SiO_4 tetrahedra are identical, having three bridged oxygen atoms each. It follows, then, that talc should greatly prefer Mg^{2+} relative to Fe^{2+}. That is the case in nature, as our data on page 332 have revealed.

By considering the electronic structures in the SiO_4 tetrahedron, we have on theoretical grounds virtually concluded that metasilicic "acid" is somewhat stronger than orthosilicic "acid" and that the "acids" corresponding to still more polymerized silicates are increasingly stronger. (By "strength" we here mean the value of the heat of formation of salts from the constituent oxides, see p. 336.) Fortunately, there exist among the very meager thermochemical data on silicates a few values which may be used to check our conclusion. Sahama and Torgeson (1949) have measured the heats of formation of Mg_2SiO_4 and $MgSiO_3$ from the oxides:

$$2MgO + SiO_2 \rightarrow Mg_2SiO_4 - 15.12 \text{ kcal.},$$
$$MgO + SiO_2 \rightarrow MgSiO_3 - 8.69 \text{ kcal.}$$

If the average bond energy in the two silicates were the same, the heat of formation of forsterite should be exactly twice that of enstatite (disregarding a small entropy term) because forsterite has twice as many Mg-O-Si bonds as has enstatite. As we see, however, the heat of formation of enstatite is more than half that of forsterite. Consequently, the metasilicic "acid" is stronger than orthosilicic "acid," and our theoretical conclusions are confirmed by experiments.

With reference now to the more complex "acids" corresponding to the double-chain silicates and the sheet silicates, we have little experimental data available as yet. But it is interesting to note that the dissociation constant of "colloidal silicic acid" is much larger than that of other acids (table 5). Although the "colloidal silicic acid" hardly corresponds to a definite Si-O framework, it is evident that this acid has a polymerized "molecule" with many Si-O-Si bridges. The fact that this acid is much stronger than the simple ortho-acid is therefore in excellent agreement with our theoretical conclusions.

No quantitative information exists on the heats of formation of anthophyllite and talc from the oxides. But the study of these minerals in rocks has revealed that the following reactions are exothermic (i.e., they proceed with dropping temperature):

$$\underset{\text{enstatite}}{7MgSiO_3} + SiO_2 + H_2O \rightarrow \underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} - \Delta H_1,$$

$$\underset{\text{anthophyllite}}{3Mg_7Si_8O_{22}(OH)_2} + SiO_2 + H_2O \rightarrow \underset{\text{talc}}{7Mg_3Si_4O_{10}(OH)_2} - \Delta H_2.$$

It follows, then, in combination with Sahama's results above, that the heat of formation from the oxides increases in the following sense if reckoned per gram atom magnesium in the silicates:

$$\Delta H_o < \Delta H_s < \Delta H_d < \Delta H_{ph},$$

where the subscripts o, s, d, and ph stand for ortho-, single-chain, double-chain, and phyllosilicates. Although the water content of anthophyllite and talc introduces some uncertainty, the trend of the values of the heats of formation of the several silicates is in agreement with our conclusion as to the strength of the different silicic acids.

TABLE 7

HEATS OF FORMATION OF CALCIUM BORATES FROM OXIDES

Compound	Heats of Formation (Kcal/Mol)
Orthoborate $\frac{1}{3}Ca_3(BO_3)_2$	20.9
Pyroborate $\frac{1}{2}Ca_2B_2O_5$	25.0
Metaborate $Ca(BO_2)_2$	32.1
Double-chain metaborate CaB_4O_7	41.0

Borates are similar to silicates, in that both may have varying degrees of polymerization. It is illuminating in this connection to note that the heats of formation of borates from oxides increase with increasing number of B-O-B bridges in the structure, as shown in table 7. This is another support for our theory of the bonding energy in silicates.

Let us focus our attention on the fact that in double-chain silicates there are two different types of nonbridging oxygens which can form (ionic) bonds with metal ions. One belongs to the pyroxene-type tetrahedra, the other to the talc-type tetrahedra. We shall denote them O_p' and O_t', respectively. It appears that the octahedral sites for Mg, Fe, etc., in anthophyllite are different, in that, for example, some of them have four O_p' and two O_t' neighbors; others have two O_p', two O_t', and two (OH) neighbors (Warren, 1933). Our considerations would require that the two octahedral sites in anthophyllite are not uniformly occupied by magnesium or iron but that the sites with two O_p', two O_t', and two (OH) neighbors preferably are filled with magnesium, those with four O_p' and two O_t' neighbors preferably with iron (or other less electropositive ions of corresponding size). (There are reasons to believe that OH plays a rather passive role in this respect and would not discriminate appreciably between Mg and Fe, see below.) E. J. W. Whittaker (1949) has made a thorough study of an amphibole and has also determined the distribution of iron and magnesium in the several positions. Whittaker's results show that the sites with but two O_p' neighbors prefer magnesium (72 per cent Mg, 28 per cent Fe), the sites with four O_p' neighbors having more iron (65 per cent Fe, 33 per cent Mg, 2 per cent Al). These empirical results are an excellent check on the theory presented here.

Whittaker also found with detailed work that the Si-O bond lengths vary, the Si-O′ being 1.59–1.60 Å, Si-O″-Si being 1.65–1.66 Å. This is in good harmony with the theory that Si-O″-Si is more ionic and single and Si-O′ more covalent and double.[7]

THE EFFECT OF (OH) ON THE Mg-Fe DISTRIBUTION

So far, the major variation considered in the silicates has been in construction of

[7] It is noteworthy, however, that, in spite of the large amount of empirical data from X-ray studies of silicates, little information has been forthcoming on the type and length of Si-O bonds.

the Si-O network. Thereby, it has been possible to eliminate other variables, such as changes in chemical composition, which are also of great significance in determining the electronegativity of the nonbridging oxygen and thus are means of controlling the Mg-Fe distribution. However, it has been impossible to eliminate the influence of OH because there exist no known natural ferromagnesian silicates of the double-chain or sheet types which are anhydrous.[8] We had to accept the presence of OH groups in these silicates. Our task now will be to decide whether or not the presence of OH in the silicate structure has any appreciable effect upon the Mg-Fe distribution. According to Warren (1929), Warren and Modell (1930*b*), and others, the structure of anthophyllite and other amphiboles shows the OH group to be attached to Fe or Mg (or other ions in the octahedral sites) and to be situated between the six nonbridging O′ atoms in a Si_6O_{18} ring. The situation is the same in talc. There seems to be no strong H bond between the OH group and the neighboring oxygens, because the OH group is not paired with a certain oxygen, as is the case, for example, in serpentine, chlorite, and kaolinite, where an OH group is attached to a bridging oxygen in the Si-O framework (by means of a hydrogen bond?) (Brindley, 1951). In talc and anthophyllite it appears that the OH group enters the structure not because it is so strongly bound to the Si-O framework but because it passively follows the metal ion. On this ground one finds it reasonable that the presence of OH groups in talc and anthophyllite will not disturb the Mg-Fe distribution, which is governed by the character of the Si-O framework. In this respect it is interesting to note the relationship between OH and F, which commonly can substitute for each other in silicates. It is known that in sheet-type silicates there is a relation between the amounts of F, Mg, and Li. Micas rich in Mg and/or Li (which are partly exchangeable) are also rich in F relative to OH. This can be explained as due to the strong forces between Li and/or Mg and F as compared with the weaker bonds between Fe and F. The base exchange reactions $FeF_2 + Mg(OH)_2 \rightarrow Fe(OH)_2 + MgF_2 - 116.7$ kcal. and $FeF_2 + 2LiOH \rightarrow Fe(OH)_2 + 2LiF - 17.0$ kcal. are highly exothermic. A Mg-rich mica will have a greater affinity for fluorine than for hydroxyl groups. In the case of fluorine, however, there can be no strong valency forces between it and oxygen in the Si-O framework because there are no hydrogen atoms to make a F-H-O bond, and the affinity between oxygen and fluorine is very weak. It therefore seems that fluorine also rather passively follows the metal ion and that it is mainly the relative amounts of Fe, Mg, and Li, as well as the availability of fluorine, which determine the F/OH ratios in many micas and other hydrous silicates.

The situation is different in serpentine and chlorites, where the OH group seems to be attached to the Si-O framework by relatively strong O-H-O bonds (see Brindley, 1951). In this case the OH group tends to direct to some extent the affinity of the whole structure for Mg and Fe. It seems most reasonable that the H bond makes the oxygen atom less electronegative than does a Si-O bond. It is worthy of notice in this connection that in a base exchange reaction of Mg and Fe

[8] This fact in itself is very interesting because it demonstrates the change in bonding in the sequence: orthosilicate → single-chain → double-chain → sheet-silicates.

between hydroxyl and an acid of some strength, Mg will go to the acid, Fe to hydroxyl:

$$FeCO_3 + Mg(OH)_2 \rightarrow Fe(OH)_2 + MgCO_3 - 12.4 \text{ kcal.}$$

If, therefore, one predicts the Mg-Fe distribution in talc and serpentine, one would tentatively say that serpentine should be more ferrophile than talc. This is apparently the case in nature, although few studies have been made. It is, in any case, well known that serpentine may be rather rich in iron. There are, in fact, specific names applied to varieties of iron-rich serpentine. However, it was somewhat surprising when the iron-rich minnesotaite was found to be a talc analogue, normal talc being virtually an iron-free magnesium silicate.

That chlorites take more iron than talc is perhaps not so much due to the conditions discussed above as it is to the Al content in the Si positions, to be discussed below.

Effect of Al in Si positions on electronegativity of oxygen and on Fe-Mg distribution in silicates

There are several interesting problems connected with the substitution of Al in the SiO_4 tetrahedron. We shall confine ourselves to two questions: Why does Al enter the Si positions more and more readily as one goes from orthosilicate to tectosilicate? How does this substitution affect the electronegativity of the oxygen? Orthosilicates do not take appreciable amounts of Al in the Si positions (the fact that Yoder and Keith [1951] recently have synthesized an orthosilicate [garnet] with very much Al in the Si position is incidental and stresses only the rarity of the situation). Single-chain metasilicates may take appreciable amounts of Al in the Si positions (Ramberg and DeVore, 1951); double-chain amphiboles take still more; micas and chlorites again have, on an average, an Al/Si ratio greater than the amphiboles. Tectosilicates may take 50 per cent of Al in the Si position. It is thus apparent that increasing the degree of polymerization through –O– bridges in the Si-O framework favors the susceptibility to accept Al in the tetrahedral positions. This is well established as an empirical fact, and we shall now attempt to give the physical explanation of it. The electronegativity value of Al is 1.5; of Si, 1.8. In harmony with our previous discussion, Al will therefore tend more and more strongly to go into a structural site at the expense of Si, the more electronegative the neighboring atoms are. Now one of our most important conclusions above was that the Si-O-Si link is more ionic than the Si-O bond in an orthosilicate. One may, in other words, say that the oxygen in the Si-O-Si link exhibits a higher electronegativity toward silicon (or toward the silicon site, rather) than does the average oxygen in an orthosilicate. On the other hand, the nonbridging oxygen in a metasilicate shows a lower electronegativity toward the silicon site than does the average oxygen in an orthosilicate. This latter effect does not compensate completely for the former, and the net result is that the average oxygen in a metasilicate acts as if it is more electronegative relative to the Si sites than does the average oxygen in an orthosilicate. It follows from the theory, then, that the more strongly electropositive metal Al will prefer to enter Si positions with a maximum number of electronegative bridging oxygen neighbors. In

orthosilicates there are no such bridging oxygen atoms; in metasilicates there are two or three in each tetrahedron; in sheet-type silicates there invariably are three; in tectosilicates there are four in each SiO_4 tetrahedron. It is immediately apparent, then, that the electronegativity of oxygen around the tetrahedral sites increases from orthosilicates to tectosilicates, and it follows readily from the theory that Al will replace Si most easily in tectosilicates.

The problem of how Al in 4-co-ordination affects the valency property of

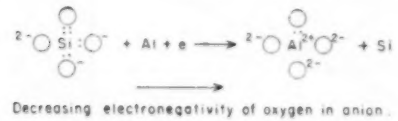


FIG. 9.—The change of electronegativity of oxygen in AO_4^{x-} when Si is replaced by Al.

oxygen and thus the Mg-Fe distribution can now be considered. When the electropositive Al is placed in the site of the more electronegative Si, the bonds to the neighboring oxygen atoms become more ionic and, in particular, of less double-bond character, and, as a consequence, the bonds from the nonbridging oxygen toward metal ions become more covalent (see fig. 9). We can therefore conclude that, by substituting Al for Si in the silicate structure, the electronegativity of the oxygen decreases and *the Fe/Mg ratio is likely to increase, all other conditions being equal.*

As a check on this conclusion, consider some silicates with varying amounts of Al in the Si positions.

Common hornblende, $Ca_{2-3}(Mg,Fe,-Al)_5(Si,Al)_8O_{22}(OH)_2$, is capable of replacing at least one-third of its Si by Al. Aluminum-rich hornblende obviously cannot exist in equilibrium with Al-poor hornblende: mix crystals are formed. It is thus impossible to determine directly the Mg-Fe distribution between aluminous and nonaluminous hornblende by rock studies. There are other ways of going about it, however. One may, for example, find a third ferromagnesian mineral as a sort of standard and compare the several varieties of hornblende with this standard in different rocks. A statistical study of the ratios Al/Si and Mg/Fe in hornblendes will also show the effect of Al in Si position upon the Mg-Fe distribution. There exist data for both these approaches.

The writer some years ago (1949) investigated the distribution of Fe and Mg

TABLE 8

Mg^{2+} AND Fe^{2+} IN COEXISTING ORTHORHOMBIC PYROXENE AND ALUMINOUS HORNBLENDES

Sample	Mg/Fe in Hornblende	Mg/Fe in Pyroxene
2,042	40/60	53/48
3,618	47/53	58/42
X Hbg.	48/52	59/41
3,766	50/50	56/44
2,148	50/50	61/39
Hbg. 4	47/53	53/47
Hbg. 2	48/52	58/42
37,711	77/23	82/18
2,188	40/60	55/45
2,074	50/50	62/38
2,016	53/47	52/48
2,129	62/38	62/38
3,310	58/42	66/34
Hbg. 1	59/41	64/36

in hornblendes comparatively high in Al and in coexisting rhombic pyroxenes. As seen from table 8, the hornblendes are decidedly higher in iron than the pyroxenes. This is very informative when considered in relation to the distribution in Al-free anthophyllite and pyroxene (table 1). The two cases fit the theoretical conclusion excellently, provided that we can assume that Al-free calciferous horn-

blende and Al-free anthophyllite have nearly the same tendency to discriminate between Mg and Fe. As they have virtually the same crystal structure, this last assumption seems reasonable.

A. F. Hallimond (1943) has compiled about 200 analyses of calciferous hornblendes. His data are abstracted in figure 10 and arranged according to the percentage of Al in the Si positions. The writer has put them in groups such that each group comprises the analyses within the following limits:

(Al_0Si_8); $(Al_{0.25}Si_{7.75})$; $(Al_{0.50}Si_{7.50})$; $(Al_{0.75}Si_{7.25})$; $(Al_{1.00}Si_{7.00})$; $(Al_{1.25}Si_{6.75})$; $(Al_{1.50}Si_{6.50})$; $(Al_{1.75}Si_{6.25})$; $(Al_{2.00}Si_{6.00})$; $(Al_{2.25}Si_{5.75})$.

Hence there are nine groups. In each group the amount of Al is averaged, as are the Fe/Mg ratios. Trivalent iron is disregarded as well as other constituents in the Mg-Fe sites. Figure 10 is the result and shows a decidedly positive relation between the amount of Al in the Si position and the Fe/Mg ratio, as anticipated on theoretical grounds.

C. Rabbitt in 1948 made a thorough study of more than 45 analyzed anthophyllites. The relations between Al content in the Si positions and the Mg/Fe ratios are plotted in figure 11. The fact that a high Al/Si ratio favors Fe in the octahedral sites is also evident here.

In attempts to reveal the relation between optics and composition, numerous chlorite analyses were compiled by A. N. Winchell in his textbook on mineralogy (1951). His diagram is striking, in that the corner for chlorites high in Fe and low in Al is not populated. A positive correlation between Fe and Al in the Si posi-

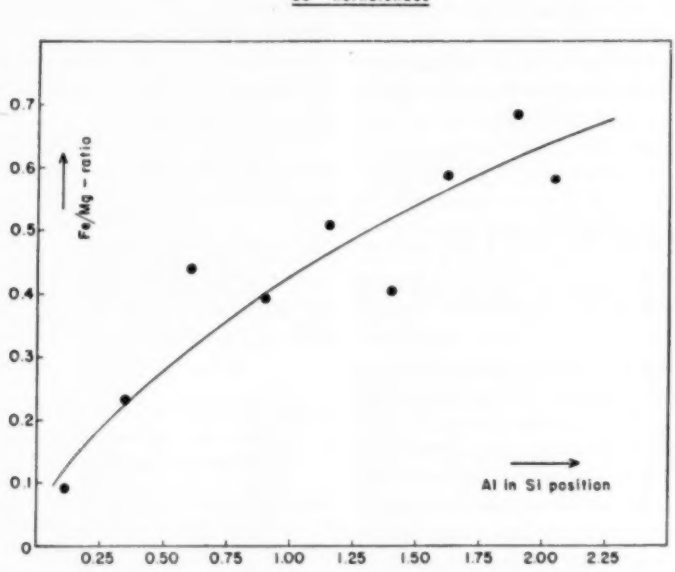


FIG. 10.—Relationship between the Fe/Mg ratio and Al in the silicon positions in calciferous hornblendes. The figures on the abscissa mean the number of Al per eight Al and Si in the $(Si,Al)_8O_{22}$ anion.

tions is again apparent. It is also informative that chlorites with some Al in the Si site have, on the average, higher Fe/Mg ratios than coexisting actinolitic hornblendes with no, or very little, Al in the Si sites. Table 9, from unpublished data of DeVore, shows this relation. However, although chlorite is a phyllosilicate, it cannot be compared directly with talc more ferrophile than talc, even if there is no aluminum in the silicon positions.

Consider now the common mineral biotite. This mineral is known to be built of a talc-type Si-O framework, differing from talc chiefly in two respects: (1) one-third to four-ninths of the silicon is replaced by aluminum; and (2) the talc-type Si_2O_5 sheets have interposed large

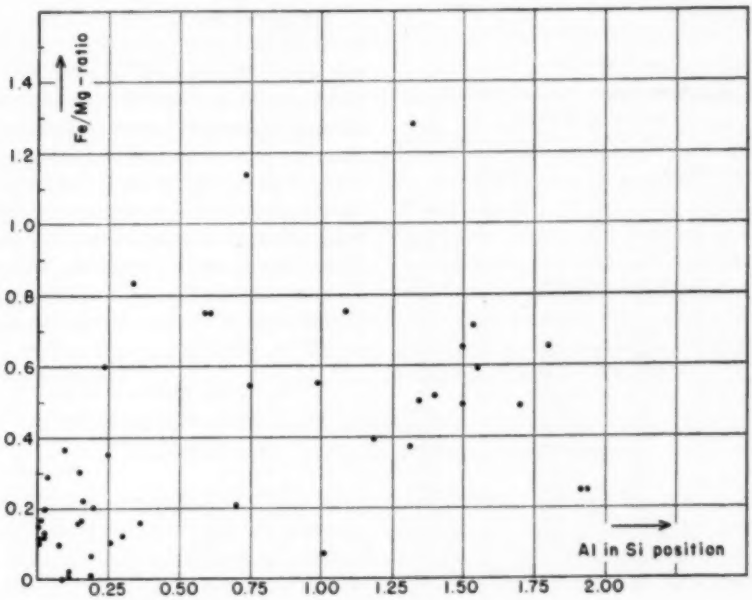


FIG. 11.—Relationship between Fe/Mg ratio and Al in the silicon position in anthophyllites

because in chlorites about half of the Mg-Fe positions are surrounded by six OH groups, as in brucite. The Mg/Fe ratio in these sites is certainly not determined by the electronegativity of the oxygen in the Si_2O_5 framework. Most likely, the octahedral sites in the brucite layer are more ferrophile than the octahedral sites surrounded by oxygen belonging to the SiO_4 tetrahedra (see the discussion on p. 343). For this reason chlorites and serpentine most likely are

cations (K^+) surrounded by bridging oxygen (O'') only. It should hardly be necessary to offer proof for the statement that biotite is much more inclined to take Fe than is talc; every petrologist is familiar with this fact. The writer has a few scattered data on the mutual distribution of Fe and Mg in biotite and coexisting silicates (table 10). It is seen that biotite actually has a larger "desire" for Fe than its sheet type of structure should require. It is true that the relatively high Al con-

tent of biotite, which is a necessary property of the mineral in order to make it electrically neutral, gives it greater affinity than talc for ferrous iron. This may be the main explanation, but it also is possible that the effect of the ionic bond between potassium and bridging oxygen changes the bonds inside the tetrahedron and hence also the electron affinity of the nonbridging oxygen attached to iron and magnesium.

TABLE 9

Fe-Mg DISTRIBUTION IN ACTINOLITES AND CHLORITES*

ACTINOLITE		CHLORITE	
γ	Mg/(Mg+Fe)	γ	Mg/(Mg+Fe)
1.643	0.81	1.602	0.70
1.640	.85	1.597	.75
1.648	.75	1.604	.65
1.636	.90	1.593	.75
1.633	.93	1.595	.75
1.645	.80	1.600	.70
1.643	.80	1.595	.75
1.642	.82	1.601	.80
1.652	.70	1.595	.75
1.638	.87	1.600	.80
1.643	.81	1.597	.75
1.641	.82	1.605	.65
1.648	.75	1.592	.80
1.638	.87	1.598	.75
1.642	0.81	1.000	0.70
Average	0.82	Average	0.74

* Unpublished data of G. DeVore.

The amounts of Al in Si positions in calciferous hornblende and in diopsidic pyroxene present a problem. These two minerals have the same Si-O structures as have anthophyllite and rhombic pyroxenes, respectively (double and single Si-O chains). One should therefore also expect that diopsidic pyroxene would take, on an average, about as much Al in the Si sites as does rhombic pyroxene and that common calciferous hornblende would take about the same amount of Al as does anthophyllite. But this is not quite the case. Calciferous hornblende, $Ca_{2-3}(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$, usually takes somewhat more Al in the Si site than does anthophyllite (Hallimond, 1943; Rabbitt, 1948). It is still more apparent that diopsidic pyroxene takes more Al than does the orthorhombic form (Rankama and Sahama, 1949; Muir, 1951).

A study of the structure of the several minerals (Warren and Bragg, 1928; Warren, 1929; Warren and Modell, 1930*a*, *b*; Warren and Biscoe, 1931) makes the following explanation tempting. In orthorhombic pyroxenes and in anthophyllite, some of the bridging oxygen atoms in the Si-O-Si link are not in contact with metal ions, whereas in diopside all the oxygen atoms are in contact with Mg, Ca, or Fe. In common calciferous hornblende there is also a greater percentage of the oxygen atoms in contact with Mg, Fe, or Ca than in anthophyllite. When oxygen is in contact with any metal ion, a certain polarization will take place, such that the O-Si bond on the opposite side of the oxygen will be reduced in double-bond character and rendered more ionic. In diopside and common hornblende, for this reason, more O-Si bonds are made ionic than in rhombic pyroxenes and anthophyllite.

TABLE 10

Fe-Mg DISTRIBUTION IN BIOTITE AND PYROXENE: Mg/(Fe + Mg)*

Biotite	Hypersthene
0.15–0.30	0.55
.20– .35	.54
.30– .45	.66
.65– .75	.83
.30– .45	.75
.40– .52	.80
.30– .45	.77
0.30–0.52	0.80

* Data from gneisses of West Greenland; determined by optical investigation.

The more ionic the O-Si bond, the more readily Si is substituted for by Al, and it appears that we can theoretically account for the small deviation in Al/Si ratio in the minerals here considered. Before this explanation can be considered valid, however, it must be checked quantitatively, particularly because the polarizing powers of Ca^{2+} and Mg^{2+} are considerably different.

NOTES ON MISCELLANEOUS FERROMAGNESIAN MINERALS

Cordierite, staurolite, and garnet are important ferromagnesian minerals which should be considered.

It is established that coexisting cordierite and garnet behave differently toward iron and magnesium, garnet being ferrophile, cordierite magnesiophile (Folinsbee, 1941). This is in harmony with the preceding discussion, because garnet is an orthosilicate, cordierite a Si_6O_{18}-type metasilicate.

It is observed that staurolite is a rather pure ferro(ferri-)silicate without a magnesium analogue. However, as it is established that iron is in 4-co-ordination in staurolite (Schiebold and Cardoso, 1929), it is likely that magnesium cannot proxy. Whereas iron has a certain tendency to build four covalent bonds, magnesium has no such ability.

THE DISTRIBUTION OF CALCIUM AMONG VARIOUS SILICATES

We have so far considered only the distribution of Mg and Fe among silicates. We shall now proceed to several other common elements, in particular Ca, K, Na, and Li. Let us start with calcium. This element is much more electropositive than magnesium (see table 2) and should therefore preferably combine in the more "acidic" silicate structures, or those with the most electronegative oxygen. That is, the reaction below should be displaced toward the right:

$$\text{Ca-orthosilicates} + \text{(Fe,Mg)-metasilicates} \rightarrow \text{Ca-metasilicates} + \text{(Mg,Fe)-orthosilicates} - \text{energy}.$$

The tendency symbolized by this reaction is clearly demonstrated among natural minerals. Orthosilicates of calcium are rare indeed, but single- and double-chain metasilicates rich in calcium are among the most common silicates (diopsidic pyroxenes and "common" calciferous hornblende as well as wollastonite). Among the generally rare calcium orthosilicates, larnite, Ca_2SiO_4, and monticellite, $CaMgSiO_4$, are the best known. We will not consider here the complex calcium-aluminum silicates which belong to the orthosilicate type: grossularite, epidote, and sphene. The mineral assemblages in rocks show that the following possible mineral interactions are displaced almost invariably toward the right:

$$\underset{\substack{\text{monticellite}\\\text{orthosilicate}}}{CaMgSiO_4} + \underset{\substack{\text{orthopyroxene}\\\text{metasilicate}}}{2MgSiO_3} \rightarrow \underset{\substack{\text{olivine}\\\text{orthosilicate}}}{Mg_2SiO_4} + \underset{\substack{\text{diopside}\\\text{metasilicate}}}{CaMgSi_2O_6} - \text{energy}.$$

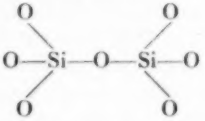
The electropositive calcium goes spontaneously from the orthosilicate toward the metasilicate, and part of the less electropositive magnesium is displaced from the metasilicate toward the orthosilicate.

$$\underset{\text{larnite}}{Ca_2SiO_4} + \underset{\text{rhombic pyroxene}}{4MgSiO_3} \rightarrow \underset{\text{diopside}}{2CaMgSi_2O_6} + \underset{\text{olivine}}{Mg_2SiO_4} - \text{energy}.$$

In this system the right-hand side with Ca in the metasilicate and Mg in the orthosilicate is invariably the stable assemblage in rocks.

$$\underset{\substack{\text{larnite}\\\text{orthosilicate}}}{Ca_2SiO_4} + \underset{\substack{\text{diopside}\\\text{metasilicate}}}{CaMgSi_2O_6} \rightarrow \underset{\substack{\text{wollastonite}\\\text{metasilicate}}}{2CaSiO_3} + \underset{\substack{\text{monticellite}\\\text{orthosilicate}}}{CaMgSiO_4} - \text{energy}.$$

This reaction in nature is also displaced toward the right, although commonly a part of the wollastonite will react with the monticellite to form $Ca_2MgSi_2O_7$, akermanite, which is a pyrosilicate of the following anion structure:



thus having electrochemical properties halfway between orthosilicate and metasilicate.

For geometrical reasons it does not seem possible to construct a double-chain silicate where the large calcium is the only cation. The common hornblende has different cation sites, some of which have eight oxygen neighbors, others six. Calcium can be placed in the large, but not in the small, holes. Therefore, a silicate of the formula $Ca_7Si_8O_{22}(OH)_2$ does not exist. The following stability relation shows, nevertheless, that the double-chain silicate has greater chemical affinity to calcium than has the single-chain metasilicate:

$$\underset{\text{diopside}}{2CaMgSi_2O_6} + \underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} \rightarrow$$

$$\underset{\text{tremolite (hornblende)}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{enstatite}}{4MgSiO_3} - \text{energy}.$$

The left-hand association is very rare in rocks, but the right-hand side is common in basic gneisses and amphibolites.[9]

The large size of the calcium ion as compared with Mg and Fe becomes very important for the interpretation of the lack of Ca in most sheet-type silicates. Talc, serpentine, chlorites, and some micas can be considered as built of Si_2O_5 sheets, sandwiched with rather closely packed O and OH layers, in which the small ions Mg, Fe, Li, and Al exist in 6-co-ordination. Even with the small Mg (and Fe) ions the O-OH layers are commonly a little too large to fit exactly on the Si_2O_5 sheets and strain and bending occur, as, for example, in serpentine (Brindley, 1951). It would be completely impossible to try to squeeze the large calcium ion into the magnesium positions in these types of structure, even if the chemical affinity for calcium were very great. If the interstices among the O ions which house Mg were large enough, one would expect the electropositive calcium to be a most abundant element in sheet-type silicates.

Before proceeding, let us return to the behavior of oxygen in the Si-O framework. How an oxygen in a Si-O bridge behaves relative to a metallic ion has not yet been discussed. Yet in sheet silicates and in tectosilicates the bridging oxygen atoms become increasingly important as neighbors to cations. The Si-O-Si link is appreciably covalent in nature, with an oxygen valency angle varying somewhat. In this situation it would appear likely that the behavior of the bridging oxygen

[9] In Rabbitt's thorough study (1948) of the anthophyllite series, he does not mention a single assemblage where diopside coexists with anthophyllite.

relative to cations is different from the behavior of oxygen with but one Si-O bond. In the bridge the electrons are partly pulled over along the two bonds pointing out from the oxygen atom. For that reason the electron affinity of the oxygen must be high around the portion of the oxygen atom which is farthest removed from the two bonds toward silicon. However, the two bonds complete the electron shell of oxygen, and therefore it should have little desire to incorporate a new electron from some neighboring metal atom (this point may be discussed, for it is known that oxygen may take more than eight electrons in some compounds). By replacing some of the tetravalent silicon with trivalent aluminum, the bridging oxygen will have only seven electrons in its outer shell, and the incorporation of another electron will take place with a considerable release of energy in harmony with the high electron affinity of bridging oxygen. We therefore find it most likely that the electronegativity of bridging oxygen in a (Si,Al)-O network is even higher than the electronegativity of the nonbridging oxygen in a SiO_4 tetrahedron with three bridging oxygens (see fig. 12).

Let us now consider the position of Ca in phyllosilicates. On geometrical grounds we found it impossible to construct Ca-analogues of talc, serpentine, or chlorite, the Ca ion being too large. The Si_2O_5 sheets, however, can also be sandwiched together in such a way that bridging oxygens surround the cations, and it becomes geometrically possible to incorporate large ions like potassium, sodium, and calcium. With calcium as the large cation, the mica margarite appears: $CaAl_2(Si_2Al_2)O_{10}(OH)_2$. Because the electropositive calcium is in contact with the very electronegative bridging oxygen, one would think that margarite would be a stable mineral relative to single- and double-chain metasilicates of calcium (diopside, wollastonite, common hornblende), where calcium is surrounded chiefly by nonbridging oxygen. That this is not the case is demonstrated by the rarity of margarite in nature. There must be another reason for its relative instability. We have seen that the amount of Al which may replace Si in silicates is limited, the limit increasing with increasing numbers of Si-O-Si bridges. Comparison

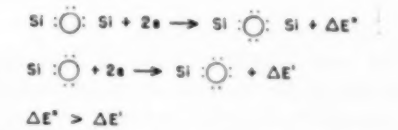


FIG. 12.—The relative values of electron affinity of bridging or nonbridging oxygen, respectively.

with other phyllosilicates indicates that a fifty-fifty Al-Si mixture, as in margarite, is close to the very limit. Other sheet silicates have considerably less Al in the Si positions (25–35 per cent for muscovite and biotite). Perhaps margarite is unstable, not because of weak Ca-O bonds, but because of weak (Al,Si)-O bonds due to the exceptionally high Al percentage in the tetrahedral sites.

The chief property of the tectosilicates is that they consist of SiO_4 tetrahedra linked together in all four corners by Si-O-Si bridges. There are no oxygens not bound to two silicons. As we have seen above, the electron affinity of oxygen in tectosilicates must be very high if some Si is replaced by Al. For that reason, the electropositive calcium finds a stable and comfortable shelter in the tectosilicate anorthite, which is the most common calcium silicate in the earth's crust. Also, other tectosilicates, such as scapolite and

some zeolites, are common calcium silicates.[10]

THE DISTRIBUTION OF ALKALI METALS IN SILICATES

In close agreement with the increase of electronegativity of oxygen through the sequence: ortho- → meta- → phyllo- → tectosilicate, the strongly electropositive alkali metals decidedly prefer to build phyllo- and tectosilicates. In particular, the alkali metals are almost invariably attached to the strongly electronegative bridging oxygen atoms in phyllo- and tectosilicates. The micas, feldspars, feldspathoids, and zeolites are by far the most common alkali minerals. The following hypothetical reaction is displaced completely toward the right:

Alkali orthosilicate + (Mg,Fe) tectosilicates →
alkali tectosilicate + (Mg,Fe) orthosilicates − energy.

We note also that there is a general tendency for increase in alkali content through the mineral sequence: olivine → pyroxene → hornblende → micas → tectosilicates. Although but small amounts (order of magnitude, 1–3 per cent) of alkali go into the common varieties of these minerals, the fact that pyroxenes commonly are somewhat richer in sodium (potassium) than is olivine and hornblendes still richer in alkali than are pyroxenes is in harmony with the electronegativity changes of the oxygen in the structures.

Lithium plays an interesting role, in that its ionic radius is similar to those of magnesium and divalent iron. For geometrical reasons, therefore, lithium tends to proxy for magnesium rather than for potassium and sodium. Also, Li has a somewhat larger electronegativity value than either Na or K (see table 2), although it is smaller than those of Mg and Fe. In view of the theory presented in this paper, one would expect that the Li/(Fe,Mg) ratio in coexisting silicates increases from olivines to micas; and one would also expect Li to build some tectosilicates, provided that it is possible to construct such silicates with so small an ion. Unfortunately, there has been little detailed study of the distribution of Li among coexisting silicates. Nevertheless, any advanced textbook in mineralogy will show that the Li ion is appreciably concentrated in common micas but in most cases is present only in traces in hornblendes or common pyroxenes. It appears, therefore, that our not too well founded general knowledge about the Li/Mg ratio in minerals is in harmony with the electronegativity values of these two elements. We shall note also that one of the most common Li minerals is the tectosilicate petalite, $Li(AlSi_4)O_{10}$. It would be conceivable now that Mg (or divalent iron) could build a similar tectosilicate, $Mg(Al_2Si_3)O_{10}$, because of the similar ionic radii. But such magnesium (or ferro-) tectosilicates do not exist. There are no geometrical reasons why magnesium and iron are unable to build at least this tectosilicate. Their electronegativity values are too high.

[10] One should note that the Al-Si replacement, which must necessarily accompany the entrance of Ca, works toward a decrease in stability of the whole structure in a manner similar to that mentioned in the discussion of margarite. However, in tectosilicates Al enters the Si position more readily than in phyllosilicates, so that the 50 per cent Al in the Si sites in anorthite does not weaken the structure by the same amount as does the 50 per cent of Al in margarite.

MELTING POINTS OF SILICATES, AND SOME DISTRIBUTION RELATIONSHIPS BETWEEN SILICATES AND OXIDES

At first one may conclude that the melting point of a silicate or other salt is lower, the weaker the electrostatic bond energy between the cation and the surrounding oxygen ions. Goldschmidt (1937) considered this a guiding principle, and one of his postulates was, therefore, that, among silicates with different cations of the same charge, the melting point should decrease with increasing size of the cations. Available data from silicates and other oxysalts show that Goldschmidt's prediction in this matter was not so successful as so many of his others. There are, indeed, many cases of the relative melting points of corresponding salts of different bases being opposite to the simple assumption of Goldschmidt (table 11). Such a state of affairs, which has recently been noted without further explanation by J. R. Goldsmith (1949) and M. J. Shaw,[11] is readily explained in view of the theory of chemical bonds in salts as discussed in this paper. The weak electrostatic energy between the larger cations and surrounding oxygen ions makes the covalent bonds inside the anion stronger. The increase of strength of the latter bonds, measured in terms of energy, is greater than the decrease of strength of the bindings about the cation (see fig. 2). For that reason it is a dangerous oversimplification to consider only the cation-oxygen bonds in a salt when

TABLE 11

MELTING POINTS OF SOME OXYSALTS*

Salt†	Temperature (° C.)	Salt†	Temperature (° C.)
$LiNO_3$	252 ± 0.2	$K_2Si_4O_9$	770 ± 1
$NaNO_3$	310	$Rb_2Si_4O_9$	957 ± 4
KNO_3	333		
		$LiAlSiO_4$	1,388
$NaPO_3$	617	$NaAlSiO_4$	1,526
KPO_3	810	$KAlSiO_4$	1,755
Na_2MO_4	687	$Ca(NO_3)_2$	561
K_2MO_4	919	$Ba(NO_3)_2$	592
Li_3PO_4	857	$MgSiO_3$	1,524
K_3PO_4	1,340	$CaSiO_3$	$1,540 \pm 2$
		$SrSiO_3$	$1,580 \pm 4$
$Li_2B_2O_4$	843	$BaSiO_3$	$1,604 \pm 4$
$K_2B_2O_4$	950		
		Mg_2SiO_4	$1,890 \pm 20$
$Li_2B_8O_{13}$	730	Ca_2SiO_4	$2,130 \pm 20$
$Na_2B_8O_{13}$	816		
$K_2B_8O_{13}$	857	$CaAl_2O_4$	$1,600 \pm 5$
		$SrAl_2O_4$	2,015–
$Na_2Si_2O_5$	874 ± 3	$BaAl_2O_4$	$2,000 \pm 40$
$K_2Si_2O_5$	$1,045 \pm 1$		
$Rb_2Si_2O_5$	1,155	$CaAl_2Si_2O_8$	1,553
		$SrAl_2Si_2O_8$	1,660
		$BaAl_2Si_2O_8$	1,720

* Data from *Handbook of Physical Constants* (1942) and *Data on Chemicals for Ceramic Use* (1949).

† Ionic radii (all in Å): $Li^+ = 0.78$; $Na^+ = 0.98$; $K^+ = 1.33$; $Rb^+ = 1.49$; $Mg^{++} = 0.78$; $Ca^{++} = 1.06$; $Sr^{++} = 1.27$; $Ba^{++} = 1.43$.

[11] Manuscript to be published shortly.

speculations as to their melting points, etc., are the object. It is now of the greatest significance to know whether the melting means breakdown of the M-O bonds or of the A-O bonds (M = cation, A = central atom in anion). If it means breakdown of A-O bonds, the melting point should change opposite to Goldschmidt's rule; if it means breakdown of M-O bonds, Goldschmidt's rule may be valid. As seen from table 11, melting of salts to a great extent requires breaking of bonds inside the anion. In conclusion, however, it should be stressed that the relative melting points are not related to the bond energies in a simple manner; entropy of melting may be a more adequate measure.

The distribution of Fe and Mg in silicates and ionic oxides is in harmony with the theory presented in this paper. The electron affinity of oxygen in the common ionic oxide minerals like spinel, magnetite, ilmenite, etc., should be less than of oxygen in most silicate anions. Therefore, one would expect Fe to go preferably to the oxides, Mg to the silicates:

$$\underset{\text{ferrosilite}}{FeSiO_3} + \underset{\text{magnetite}}{FeFe_2O_4} \rightarrow \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{magnetite}}{MgFe_2O_4},$$

$$\underset{\text{ferrosilite}}{FeSiO_3} + \underset{\text{ilmenite}}{FeTiO_3} \rightarrow \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{geikielite}}{MgTiO_3},$$

$$\underset{\text{ferrosilite}}{FeSiO_3} + \underset{\text{spinel}}{FeAl_2O_4} \rightarrow \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{spinel}}{MgAl_2O_4}.$$

These three reactions should be exothermic and hence go to the right below certain temperature limits. In nature the first two reactions are clearly displaced to the right, and it has been determined experimentally (Sahama and Torgeson, 1949) that the second is so displaced. (Because the iron and magnesium silicates are miscible, pure enstatite will in most cases not occur together with magnetite or ilmenite; commonly the silicates on the right side of the equations contain some iron.) It is not clear from field observations whether or not the last reaction is displaced to the right. Because the silicate as well as the "aluminate" involved are mixed crystals of Mg and Fe, only a detailed investigation of the Mg-Fe distribution in coexisting silicates and spinels will give us information in this matter.

CONCLUSIONS

The distribution of metals among silicates is only partly governed by the size and charge of the ions. Very important factors are the electronegativity values of the metals and the electronegativity values of the oxygen atoms in the silicates. The latter value is changeable and increases stepwise from orthosilicates through metasilicates and phyllosilicates, having its highest value in tectosilicates. The most electropositive metals (K, Na, Cs) tend to combine with the most electronegative oxygen and therefore to build phyllo- and tectosilicates (feldspar, etc.). The most electronegative metals, on the other hand, (Fe, Mg) tend to combine with the least electronegative oxygen and hence to build orthosilicates and metasilicates. Many details of the element distribution encountered in natural minerals are accounted for by the new theory presented. It seems likely that, as new critical data become available, the theory may be refined and put on a quantitative basis to such an extent that the element distribution among minerals can be thoroughly understood and unknown details be predicted.

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REPLACEMENT AND RHEOMORPHIC DIKES[1]

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ABSTRACT

In the field, dikes formed by replacement show such features as lack of offset on transecting an earlier dike at an acute angle, bridgelike septa across the dike, an irregularity of form with a tendency toward lenticularity, and both sharp and gradational borders. Large thin sections show a prevalence of crystalloblastic textures and structures and a complete lack of flow structure or chilled borders or increase in grain size from the border inward.

Some dikes at Cornucopia, Oregon, although exhibiting crystalloblastic textures and structures, also show marked fluxion textures indicative of mass movement. These conflicting data are interpreted as follows: A continuance of more active emanations following static metasomatism may be one of the factors that caused the newly formed material to flow as a neomagma and form a rheomorphic dike.

INTRODUCTION

In a previous paper entitled "Dilation and Replacement Dikes" (1940), the writer presented criteria to distinguish orthomagmatic dikes from replacement dikes. The former were formed by injection of magma concomitant with the widening of a fissure, whereas the latter are attributed to metasomatic processes. Excellent examples of both kinds of dikes are to be seen in many localities of western United States. The diagnostic features of orthomagmatic dilation dikes, familiar to all geologists, are easily seen in the field, and the microtextures are usually sufficiently uniform for study in standard-sized thin sections. Although replacement dikes are superficially similar to orthomagmatic dikes, they exhibit different field features and different microtextures and microstructures. Because the microscopic features are by no means uniform, several ordinary thin sections are necessary for identification; and even then the comparison of these sections is not a simple matter. However, this difficulty is overcome by the use of large ($3\frac{1}{4} \times 4$-inch) lantern-slide thin sections. The making of large thin sections has been described recently by Lang and Smedes (1951).

Recent studies have also shown that some dikes, especially some of the porphyry dikes in the vicinity of Cornucopia, Oregon, exhibit features which cannot be fully explained by either magmatic injection or static metasomatic replacement. These dikes have in part sharp borders like orthomagmatic dikes and in part gradational borders like replacement dikes. They show similar contradictory evidence in large thin sections, where both crystalloblastic textures and well-defined flow structures occur side by side. The terms "mobilized replacement dike" and "rheomorphic dike" are suggested where flowage of metasomatized material is clearly indicated.

REPLACEMENT DIKES

In the field a replacement dike may usually be distinguished from an orthomagmatic dike by: (1) lack of structural evidence, such as offset, which would result from the dilation of a fissure preceding or accompanying magmatic injec-

[1] Manuscript received September 5, 1951. Presented at the April, 1948, meeting of the Cordilleran Section of the Geological Society of America, Pasadena, California.

tion; (2) lack of magmatic flow structure; (3) absence either of chilled borders or of the increase in grain size from borders inward, whereas such features would be expected in an igneous dike transecting rocks which were at a considerably lower temperature than the magma; (4) abrupt changes in width (pinches and swells) along both strike and dip of dike; (5) undisturbed relict material which preserves the same alignment (in the dike) as in the wall rock; (6) gradational borders, if present, are a distinguishing feature, but the presence of sharp borders does not necessarily invalidate a replacement interpretation. King (1948) in his study of aplite and pegmatite dikes in Nigeria has given an excellent description of nondilation dikes with sharp borders.

Many of the distinctive field features of small replacement dikes may be observed in large thin sections. These include: (1) lack of offset of transected structures; (2) bridgelike septa of country rock; (3) undisturbed inclusions and minute relict material, especially platy minerals like biotite; (4) apophyses which differ in composition from the main dike; and (5) variable composition and grain size.

Individual minerals commonly exhibit sieve structure and crenulated borders, turbid centers filled with metamorphic minerals, and other features characteristic of crystalloblastic growth. Perhaps another distinctive feature is the irregular over-all crystalloblastic texture common to small replacement bodies like dikes and even apparent in some granitic masses thousands of feet from their contacts with the country rock.

The initial stage in the development of some replacement dikes is a narrow zone of closely spaced parallel fracture planes or surfaces along which incipient mineralization (e.g., silicification, silication, and feldspathization) has taken place. Partial replacement of the intervening screens of wall rock by appropriate minerals forms the next stage. If the wall rock contains areas especially amenable to replacement, the incipient dike or veinlet may be widened to many times the width of an original fissure. In the later stages of development, with continued recrystallization replacement, most of the long, thin bands or irregular masses of country rock between two dominant fracture planes disappear in the newly formed crystalloblastic matrix of the dike, and only occasional inclusions remain as skialiths. The perfect parallelism of the microstructure of the skialiths with the structures of the wall rocks is cogent evidence of a static mode of formation rather than mass flowage of a magma. In some replacement dikes, where the schistosity of the wall rock is at right angles to the dike and where minute relict minerals extend into the dike, a mimetic growth of parallel feldspar crystals produces a comblike structure (pl. 1).

Although in the final stage of the development of a replacement dike all skialiths may have disappeared, the texture is crystalloblastic and commonly has an uneven over-all appearance, with individual minerals showing crenulated borders and exhibiting sieve structures, especially along their peripheries. Some replacement dikes have minute veinlets (usually of quartz) parallel to their borders, suggesting recurrent fracturing. Others have borders of mafic minerals due probably to the expulsion of iron and magnesium (metamorphic differentiation) during the process of granitization. Marginal basification is well illustrated by King (1948, fig. 19, p. 474) in his pa-

per on the aplite and pegmatite dikes in northern Nigeria.

Apophyses from replacement dikes show marked changes in mineral composition a few centimeters from the main dike. Transverse relict minerals crossing the apophyses with the same alignment as in the country rock are evidence of replacement rather than mass injection, which would have swept aside delicate relict material. A dike of granitic composition may have an offshoot which grades into a veinlet composed chiefly of quartz (pl. 2, *B*). This change in composition indicates a progressive mode of formation for the dike with an initial introduction of silica followed by the alkalis. Some replacement dikes from Cornucopia clearly show the earlier phase represented by a fine-grained aggregate chiefly of quartz and a later phase characterized by the crystalloblastic development of plagioclase. In these dikes and veinlets there appears to have been an intergranular penetration controlled by fractures, schistosity planes, or other zones of permeability. The presence of long, thin tabular cavities along the borders of a few of the dikes, which have not been subsequently altered, is indicative of the action of solutions rather than the injection of a magma. Successive replacement of a zone between two parallel dominant fracture planes produces a dike with well-defined sharp borders. In the final stages of formation of a replacement dike, most relict material is obliterated. Hence it is impossible to determine whether a particular dike developed along a series of parallel fracture planes or was formed by the replacement of a zone between two fractures.

Many rock types, such as aplite, pegmatite, granite, granodiorite, syenite, diorite, and various porphyritic equivalents, are found in different replacement dikes. Even within a single dike it is not uncommon to find several rock types represented. Such radical changes in mineral composition might suggest magmatic differentiation, but marked crystalloblastic microtextures and microstructures strongly indicate that these changes are the result of the complex processes of successive stages of metasomatism.

MOBILIZED REPLACEMENT DIKES

Continuation of the study of dikes at Cornucopia, Oregon, resulted in the finding of some dikes similar in appearance and composition to replacement dikes but with features akin to orthomagmatic dikes. These features include: regularity of width, prevailingly sharp borders, flow structure as indicated by drawn-out inclusions, and in many cases offsets of units in the wall rock indicative of dilation. Under the microscope, fluxion textures are prominent; most of the larger crystals show sieve structure and other features indicative of crystalloblastic growth.

In a small leucocratic granitic dike, well exposed in the bed of Pine Creek, 2 miles west of Cornucopia, features of replacement and mass flowage are both present. This dike transects a coarse gneissic rock, and at one place along one wall delicate mafic remnants retain their original alignment, which is nearly at

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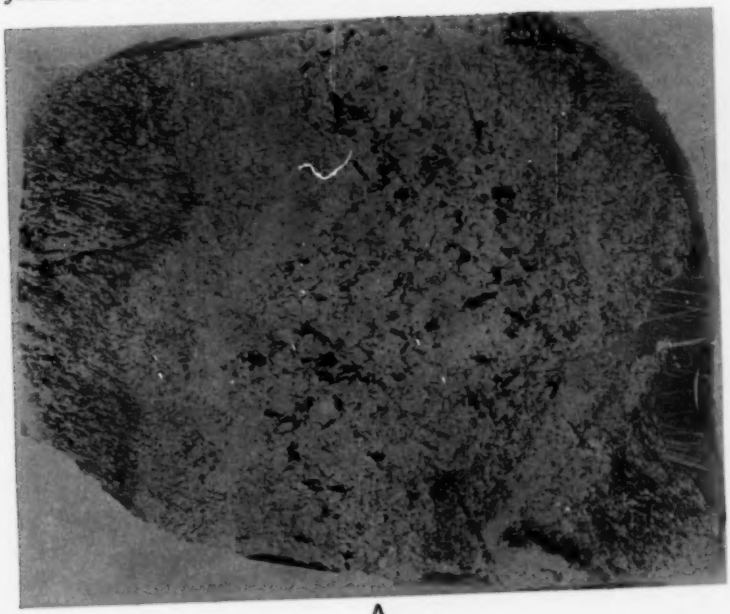
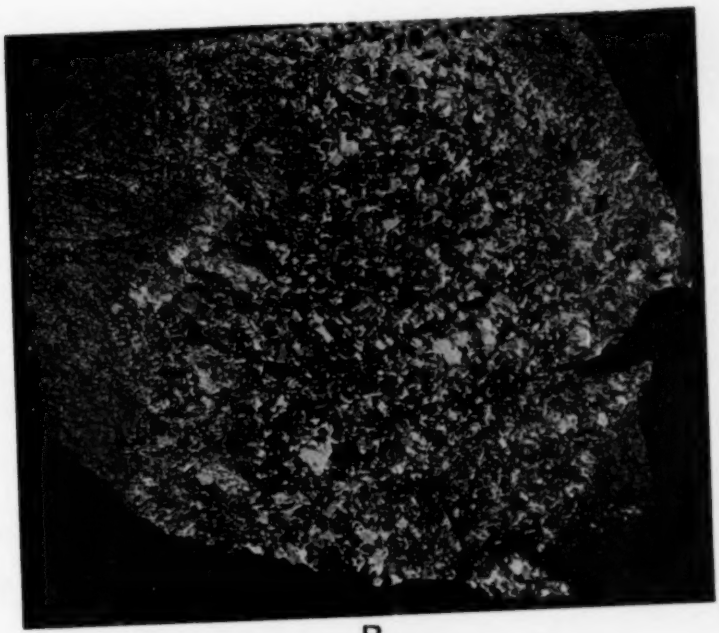
PLATE 1

Photograph of a large thin section of a specimen from a replacement dike, showing a rough alignment of plagioclase along the left border. Note that the growth is parallel to the minute relict inclusions in the dike. *A*, ordinary light; *B*, crossed polarized light.



A



B

Thin section of replacement dike

A

B

C

Thin sections and outcrop of some dikes studied

right angles to the dike, but along the opposite wall these mafic remnants swirl away from the wall and become parallel to it (pl. 2, *C*). This dike is of particular interest in that it indicates a close relationship in a small body between static metasomatism and mobilization. The flow structure as shown by the relict material also indicates that movement started along one border, and the curved pattern is indicative of a slowly moving, highly viscous mass. This dike is termed a "mobilized replacement dike."

RHEOMORPHIC DIKES

Over twenty years ago the writer described the peculiarities of some of the porphyry dikes at Cornucopia and endeavored to reconcile the evidence to the magmatic hypotheses which prevailed at that time. One of the dikes, about 2 feet wide, transects a small quartz dioritic stock which is filled with a swarm of inclusions of the schistose hornfels country rock. These inclusions (called "xenoliths" by the writer at the time) ranged from ½ inch or less to 3 or 4 inches in size. Most of the inclusions in this breccia show various stages of transformation, and the quartz dioritic matrix exhibits marked crystalloblastic textures. Larger plagioclase crystals (called "phenocrysts" by the writer at that time) are to be seen within the inclusions or along their borders and exhibit features outlined in the following quotation (Goodspeed, 1929):

> Thin sections actually show some of the plagioclase crystals which were caught in the act of forming in or near the xenoliths. In many cases, one edge of these crystals is well formed while the other has an interlocking contact with the minerals of the xenoliths. The digestion of the mafics (hornblende) of the xenolith and the simultaneous generation of the feldspar is thus plainly evident. These plagioclase crystals show a marked progressive zoning from a highly calcic variety in contact with the mafics to a very sodic outer margin. Portions of other plagioclase crystals form integral parts of hornblende crystals, actually grading into the mafic. Next to the mafic, the plagioclase is very turbid, being filled with inclusions which are mainly composed of ferruginous and kaolinitic material. It seems probable that, as the hornblende was absorbed during the growth of the plagioclase, this material was left as a residual product of the reaction. Some of the detached plagioclase phenocrysts in the matrix have turbid centers which much resemble in outline what was probably the hornblende nucleus. There is even a suggestion of amphibole cleavage cracks in the alterations material.

The dark-gray porphyry dike transecting this breccia has a very fine-grained porphyritic texture with plagioclase phenocrysts about 2 mm. in size. It has a marked vertical jointing parallel to the walls of the dike and to a finely developed flow structure. The contacts are in part gradational and in part sharp. There is no apparent change in texture of the dike from the walls inward, no glassy borders or even a finer-grained selvage. Under the microscope the phenocrysts are seen to be plagioclase, hornblende, biotite, and rarely quartz. The groundmass consists of, chiefly, feldspar, quartz,

PLATE 2

A, Photograph of a large thin section from a specimen of a rheomorphic dike with a zenolith from the granitic wall rock.

B, Photograph of a large thin section of a specimen from a granitic replacement dike. Note the ragged border, the change in mineral composition of the apophyse with minute relics of mafic minerals from the hornfels.

C, Photograph of a small mobilized replacement dike transecting gneissic granitic rock and showing included material drawn out along one border.

biotite, and hornblende, with some apatite, magnetite, and chlorite.

The plagioclase phenocrysts range in composition from calcic andesine to albite, which commonly forms the outer rim of zoned crystals. Most of the larger plagioclases have a turbid center, which is usually irregular in shape. In some of those centers distinct remnants of hornblende are visible. Many of the most turbid feldspars have very irregular outlines, whereas the clear ones are more euhedral. Two varieties of hornblende phenocrysts are present: one green in color in thin, long (2 mm.) crystals; the other stubby (0.5 mm.) and brownish in color. Some of the biotite phenocrysts consist of flaky aggregates, and their appearance suggests that they may have been derived from hornblende. Quartz phenocrysts are rare; some of them are not homogeneous crystals but are aggregates.

The following paragraphs from this paper (Goodspeed, 1929) give a brief petrographic description of the contact of the dike and the breccia and a comparison of them:

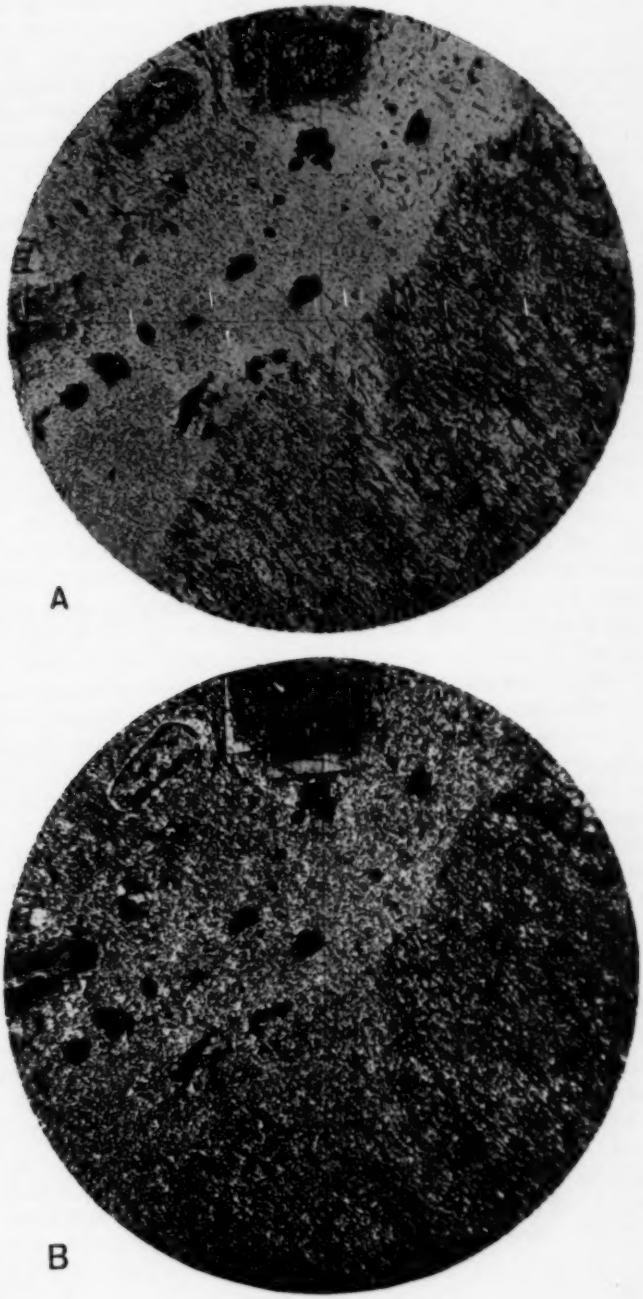
> Thin sections of the contact of this dike and the matrix are of interest. No chilling effects are present. Interlocking contacts prevail. In some parts, the demarcation between the dike and the breccia is clear, in others there is a very apparent continuation of the matrix into the dike.
>
> The essential difference between the texture of the matrix and that of the dike lies in the flow structure of the latter. Where the matrix of the breccia merges with the dike, there is a strong suggestion that the matrix was actually flowing into the dike.
>
> A comparison of the dike and the breccia, both matrix and recrystallized xenoliths, reveals striking similarities in that the kind and amounts of minerals correspond, and the same kind of feldspar with the same type of zoning and alteration appear in both. In the dike, as might be expected, some of the albitic rims have disappeared, and the labradorite centers have started to be reabsorbed. With the exception of the fluxion texture of the dike, the groundmass textures are similar. The rare quartz phenocrysts in the dike are of an aggregate nature similar to some of the blebs of quartz in the breccia.

At the time the above description was written, the writer's interpretation was that the dike magma was formed by reaction of the numerous xenoliths with the quartz diorite magma of the stock. Hence the dike was termed a "reaction porphyry." However, further detailed studies, with the aid of large thin sections, have shown that the "phenocrysts" in the fragments have all the attributes of porphyroblasts (Goodspeed, 1937) and that the "xenoliths" are relict fragments or skialiths (Goodspeed, 1948) forming a breccia in a quartz-dioritic rock of metamorphic origin. These studies have also corroborated the earlier interpretation that the mixture of inclusions and quartz diorite merged into the dike and flowed as a magma.

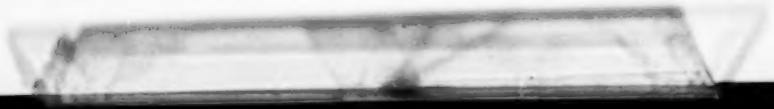
Other porphyry dikes at Cornucopia transect hornfels and recrystallized hornfelses and exhibit features similar to those just described for the dike cutting the breccia. A photomicrograph from a large thin section of the contact of one of these dikes shows small indistinct feeder veinlets originating in the recrystallized hornfels and merging into the dike (pl. 3). The flow structure, swirls of biotite flakes streamlined around feldspar porphyroblasts, clearly indicates that this material from the wall rock moved into

PLATE 3

Photomicrograph of part of a contact of a rheomorphic dike and schistose hornfels. *A*, plane light; *B*, crossed nicols.



Contact of dike and hornfels



the dike. Although most of the "phenocrysts" of these porphyry dikes appear to have originally been porphyroblasts, later growth tends to produce a more euhedral crystal approaching in form those of orthomagmatic rocks. Some stubby hornblende crystals seem to be true phenocrysts which have crystallized from the mobile mass in the dike.

Porphyry dikes identical to those just described are also found transecting granodioritic rock at Cornucopia. Although there is no direct proof of the origin of these dikes, the microtextures and structures clearly indicate that they were originally of metasomatic rather than of magmatic origin. They probably represent the flowage of feldspathized hornfels relict masses included at depth in the granodioritic rock, where higher-temperature conditions prevailed. These dikes have true intrusive relationship with the country rock, and some contain angular xenoliths of the granodioritic rock as well as xenocrysts of feldspar and quartz. The incorporation of this material appears to be merely mechanical, as no reaction features are visible (pl. 2, *A*).

In his discussion of the transformation of quartzite into granite, Backlund (1938) states: "This transformation was accompanied by increase of volume, the quartzites becoming rheomorphic with excellently developed fluidal textures, and thereby partly dynamic." This implies that rheomorphism is one of the later stages of granitization, and this assumption is borne out at Cornucopia by the porphyry dikes transecting the granodiorite. It should be emphasized that at this locality (Goodspeed, 1939) the evidence strongly favors a metamorphic interpretation of origin for the granitic rocks, as well as a rheomorphic one for some of the porphyry dikes.

Delicate flow structures seen in the groundmass of most of the rheomorphic porphyries and the marked intrusive features of the dikes transecting the granodiorite indicate mobility at the time of their formation. However, a small dike less than 1 foot in width exhibits a protoclastic structure which points to viscous flow. The outcrop of this dike is near the top of a ridge over 2,000 feet higher than the dikes previously described, and it is possible that the protoclastic structure reflects a lower temperature condition at this position in contrast to the dikes formed at greater depths.

Mobilized and rheomorphic dikes have been recognized by Misch (1949) in his geological investigations in Okanogan County in north-central Washington. At one locality northeast of Conconully, the flowage of very slightly granitized biotite schist into a dike is clearly indicated. Both the dike and the wall rock are essentially the same material, but the flow structure of the former transects the foliation of the latter. At this locality there are dilation dikes of aplite which Misch attributes to the mobilization and intrusive movement of granitized material rather than to the intrusion of original granitic magma.

It is probable that most rheomorphic dikes lacked the superheat characteristic of igneous dikes formed by hypomagmas. This may be the reason for their relatively limited lateral and vertical extent and may also account for the absence of distinctive igneous features, such as marked chilled borders and optalic metamorphism of the wall rocks.

Fragments in rheomorphic dikes might be either true xenoliths, if they have been derived from wall rocks quite different from the mobile material of the dike; or they may be mobilized skialiths where the rheomorphic rock has been directly derived from the wall rocks. It is prob-

able that many schlieren could be classified under one or the other of these two categories.

CONCLUSIONS

Replacement dikes are common features of the early stages of large-scale static metasomatism and afford one of the mechanisms for the advance of granitization. They are also formed during the retrograde stage of granitization, as is illustrated by many late aplitic and pegmatitic dikes (Goodspeed and Fuller, 1944).

Mobilization implies the movement of metasomatized material by plastic flowage. In general, however, there is not sufficient fluidity to permit the formation of crystals by fractional crystallization concomitant with the flowage. Dikes showing features of metasomatic replacement and flowage are called "mobilized replacement dikes."

Rheomorphism, used in a restricted sense, not only implies the movement of metasomatized material by plastic flow but also infers a sufficient amount of intergranular fluid to allow some minerals to form by fractional crystallization during the period of flowage. Rocks resulting from rheomorphism exhibit initial crystalloblastic textures and later, clearer, more homogeneous crystals which have separated from the intergranular solutions of highly mobile material. Flow structures are pronounced and intrusive relationships common, although relict features may be present.

Neomagmas may be considered to consist of completely metamorphosed material ranging from mobile groutlike consistency to a more homogeneous liquid or even a melt which flows easily, has intrusive relationships to the country rock, and is sufficiently fluid to permit an abundance of crystals to form by fractional crystallization during flowage and later cooling stages. Earlier crystalloblastic textures are still discernible in neomagmatic rocks. Although flow structures and later formed crystals may produce a similarity to orthomagmatic rocks, the presence of earlier minerals exhibiting crystalloblastic features and the absence of well-formed earlier pyrogenic minerals, their relics, or orthomagmatic textures serve to distinguish neomagmatic rocks from truly magmatic rocks. In an extreme case, it might be possible for a neomagma to become a liquid silicate melt, but even in this case earlier nonpyrogenic features could give a clue as to the origin of the neomagma. Such cases are similar to some examples of local ultraoptalic metamorphism. Probably certain rheomorphic dikes furnish the best illustration of a neomagmatic rock.

Rheomorphic dikes in contrast to replacement dikes are characteristic of the most intense period of metamorphism and are not common either in the early stages nor the later retrogressive stage. Rheomorphism may not be limited to small bodies like dikes, but may also affect large-scale zones which lack definite boundaries. These features have not been discussed in this paper because, in the proper sense of the term, they are not dikes.

The recognition of mobilized and rheomorphic rocks is of utmost importance to the problem of granitization. Because both the field and petrographic criteria for these rocks approach those of igneous rocks, much care must be used in an interpretation of the line of descent, i.e., whether the rock mass was derived from metasomatized material or from a differentiated hypomagma.

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CHANGE OF MELTING POINT OF DIOPSIDE WITH PRESSURE[1]

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ABSTRACT

The melting point of synthetic diopside under pressures up to 5,000 bars was found by experiment to be well represented by the equation.

$$t_m = 1391.5 + 0.01297P\,,$$

where t_m is the melting point in ° C. and P is the pressure in bars. The character of the melting curve supports the prevailing view that the melting curve rises indefinitely with depth in the earth.

The considerable volume change involved in melting is emphasized in a quantitative review of the process of magma production and extrusion.

INTRODUCTION

It is known that pressure raises the melting point of most minerals. Furthermore, the initial rate at which pressure raises the melting point can be estimated from thermodynamic values obtained at atmospheric pressure. For higher pressures, it has been of interest to speculate as to the character of the melting curve. The question had been whether the melting curve rises to a maximum, ends in a critical point, rises asymptotically to a specific temperature, or rises indefinitely. Although it is now generally recognized that the melting curve rises indefinitely, the change of melting point with pressure at higher pressures can be obtained only by direct measurement. Many organic and some inorganic compounds have been investigated, but none of them is of direct interest to geologists. Therefore, one of the important rock-forming minerals, diopside, was chosen and its change of melting point with pressure was investigated.

Diopside was selected for investigation because it melts and freezes readily and at a temperature more easily attainable experimentally than that for most other important nonhydrous minerals. In addition, diopside or, more generally, augite is a common constituent of basic rocks, which are believed to form the principal part of the deepest portions of the earth's crust. The effect of pressure on the melting point of diopside is also of exceptional interest because the large volume change between solid and liquid (calculated from the density of crystal and of corresponding glass) should give rise to a large pressure effect. For these reasons experimental values of the melting point of diopside at pressures up to 5,000 bars have been obtained.

DESCRIPTION OF APPARATUS

In brief, the apparatus consists of a large steel cylinder, capable of withstanding over 15,000 bars, which is fitted internally with an electrical resistance furnace. The measurement of the melting point was made at various pressures by a combination of the heating curve and differential thermal methods. Some details will be presented of the pressure system and method of pressure measurement; the furnace assembly and method of temperature measurement; the mechanism used in establishing a linear heating rate in the furnace; and the thermal block in

[1] Manuscript received April 19, 1951.

which the sample and a reference material are contained.

PRESSURE SYSTEM AND PRESSURE MEASUREMENT

The pressure is applied by compressing argon gas into the internally heated pressure vessel. Pressures up to 2,000 bars are obtained directly, using a commercial pump; higher pressures are obtained by means of an intensifier. The pressure is measured indirectly by the change in resistance of a manganin-wire coil. The pressure-sensitive coil is calibrated at the known freezing points of CCl_4 and Hg under pressure. Further details of the pressure system and method of pressure measurement may be found in a previous publication (Yoder, 1950, pp. 827–830).

FURNACE ASSEMBLY

A refractory-porcelain tube, 6 inches long with $\frac{1}{2}$-inch inside diameter, is wound externally with 0.8-mm. platinum wire. The furnace is centered by ceramic spacers in a nickel tube, which fits closely into the horizontal, gas-tight, pressure cylinder.

The furnace winding was covered with a thin film of cement (Norton RA No. 518) and wrapped with platinum foil (thickness, 0.05 mm.), which acts as a radiation shield. The cement was prefired and the cracks refilled, to increase the efficiency of the furnace. No further insulating material was used around the furnace. All free space within the furnace was filled with alundum (Norton crystalline alumina) to decrease convection. Approximately 2.5 kw. were required to reach 1,400° C. under pressure.

Because no insulation was used around the furnace, the temperature of the pressure vessel rose considerably. Water-cooling the surface of the pressure cylinder reduced the temperature of the ends of the cylinder to a value near that of the room.

HEATING-RATE MECHANISM

The furnace temperature was controlled roughly by a Variac (variable transformer). The finer control necessary for establishing a linear heating rate was obtained by mechanically varying the resistance of a coil in series with the furnace. The mechanism consisted of an insulated drum on which was wound a large-capacity, half-ohm resistor. The helically wound coil, tracked by movable contacts, was rotated by a variable-speed motor. By varying manually the speed of rotation, resistance could be reduced in the furnace circuit at any desired rate. In this manner a linear heating rate was established in the furnace, irrespective of the greatly varying power requirements.

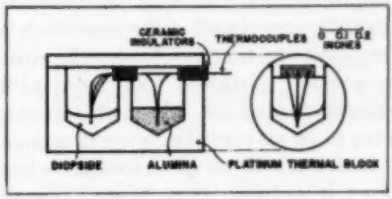

FIG. 1.—Arrangement of thermocouple junctions in platinum thermal block containing diopside sample and alumina reference.

TEMPERATURE MEASUREMENT

Platinum versus platinum-10 rhodium thermocouples were used to measure the temperature at the center of the diopside sample and the difference in temperature between the diopside sample and the alumina reference. The arrangement of the junctions in a thermal block is shown in figure 1. The use of a large thermal block (36 gm.), a long zone of even heating, and the filling of all free space within the furnace reduced the total variation in temperature within the block to less than

0°.1. Calibration of the thermocouples prior to use in the pressure cylinder was not considered necessary, because a base point was established for each series of runs, a method which will be described in a following section. The errors due to the unknown effect of pressure on the e.m.f. of the thermocouple and those due to the electrical conductivity of the melt in which the temperature is measured are assumed to be negligible in these experiments.

THERMAL BLOCK

Approximately 80 mg. of synthetic diopside were placed in one receptacle of the platinum thermal block; the other receptacle contained an equivalent amount of alumina. Although this may seem to be an exceedingly small amount of material with which to measure a heat effect, it is obvious from figure 3 that the amount used is adequate. In addition, several satisfactory experiments were performed in a slightly different way with amounts as little as 10 mg. The only variation in these latter experiments was that the diopside was contained in a cone of platinum wire gauze which was spot-welded at the apex to the bottom of its usual receptacle in the thermal block.

The diopside melt has comparatively low viscosity and, in addition, apparently has very strong adhesive force under pressure. On several occasions with earlier designed thermal blocks, the liquid diopside under pressure crept up the walls of the container and along the thermocouple wires, dissolved the refractory-porcelain insulators, and entered the alumina receptacle. When this took place, the melting point of the material remaining in the diopside receptacle was lowered considerably by contamination, and therefore that setup was discarded. The use of a thermal block of the design shown in figure 1 and a small sample gave satisfactory results.

MATERIALS USED

The synthetic diopside used in this investigation was very carefully prepared by J. F. Schairer from pure $CaCO_3$ (less than 0.001 per cent alkalies), SiO_2 (less than 0.03 per cent total impurities), and MgO (about 0.2 per cent alkalies). Ideally, the temperature throughout the time interval required for melting should be constant; however, even when the purest available constituents have been used, this condition has not been observed for any silicate. The temperature change during melting was found by the quenching method to be of the following magnitude for three specific silicates prepared by J. F. Schairer (personal communication): pseudowollastonite: 1° C.; diopside: 4° C.; and anorthite: 16° C. (As explained below, these large temperature changes during melting should in no way be regarded as reflecting adversely on the accuracy of the melting-point measurements.) According to White (1909), the temperature changes during melting are due to the presence of impurities. For pseudowollastonite, whose two constituents can be obtained very pure, the melting interval is very small. In the case of diopside the chief source of impurities, mainly alkalies, is in the MgO used in the preparation. In fact, J. F. Schairer (personal communication) has made diopside from different lots of MgO of chemically pure grade; the differences in melting point could be attributed directly to the difference in amount of impurities in the MgO. He has found that this method of testing the purity of a particular batch of MgO is as sensitive as a chemical analysis.

The melting point is defined as that temperature at which liquid and crystals

are in equilibrium. In practice the liquidus temperature has been determined by observing that temperature at which the last crystal melts. Melting points of silicates determined in this way can be reproduced within 0°.5 C. However, the first formation of liquid may be hundreds of degrees below this point. Take, for example, a simple binary system, diopside—X, which has a eutectic at 1,000° C. (fig. 2). If there be only 0.001 per cent X in the crystalline material, liquid will appear at 1,000° C., but the last crystal will melt only slightly below 1,391°.5 C.

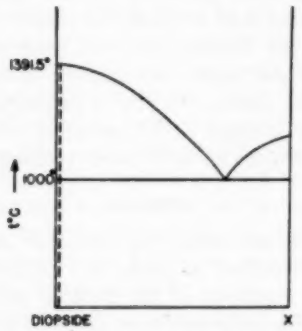

FIG. 2.—Hypothetical binary system, diopside-X

Therefore, small quantities of impurities have only a slight effect on the liquidus temperature. Even though the diopside used is of the highest purity, a small change of temperature during melting is to be expected.

The melting point of synthetic diopside was determined by Day and Sosman (1910) as 1,391°.2 ± 1°.5 C. on the gas-thermometer scale, using the heating-curve method. This value was converted by Adams (1914) to 1,391°.5 ± 1°.5 C. on the thermodynamic scale and is now used as a calibration point for thermocouples at the Geophysical Laboratory.[2]

The alumina which was used as a reference substance for the differential thermal effects was obtained from the Norton Company. It was labeled 200 mesh, electrically fused, crystalline alumina, especially prepared for carbon determinations.

PROCEDURE

After assembly of the apparatus, the melting curve of diopside was run at atmospheric pressure in the following manner. The temperature of the diopside was brought to within 50° C. below the melting point and a heating rate of 8°–12°/min was established. Alternate readings of the temperature of the diopside and of the difference in temperature between diopside and the reference substance,

[2] The conversion, according to L. H. Adams (personal communication), is based on the relation

$$\frac{T}{T_0} - \frac{\theta}{\theta_0} = \frac{I_v \theta}{P_0},$$

in which

T = Gas thermometer temperature,

$T = T_0 \frac{P}{P_0}$,

$T_0 = \theta_0$ = Temperature of the freezing point of H_2O,

P = Pressure of gas thermometer at temperature T,

P_0 = Pressure of gas thermometer at temperature T_0,

θ = Thermodynamic temperature

$$I_v = \int_{\theta_0}^{\theta} \frac{\lambda d\theta}{\theta^2},$$

where

$$\lambda = \left(\frac{\partial E}{\partial V}\right) = \theta \left(\frac{\partial P}{\partial \theta}\right)_V - P,$$

E = Internal energy,

from which any thermodynamic temperature can be computed for any gas-thermometer temperature and vice versa. In 1922 Day and Sosman (pp. 31–32) gave the melting point of diopside on the thermodynamic scale as 1,391° ± 2° C., with the comment that "the corrections to convert readings on the constant-volume gas scales to the thermodynamic scale at 1,000° and higher are very uncertain. The correction to the constant-volume nitrogen scale at initial pressure 500 mm. is probably of the order of magnitude of +0.5° or less at 1,200°."

crystalline alumina, were made every 15 seconds. As soon as was practicable after melting, the temperature was dropped to a temperature approximately 100° C. below the melting point, in order to crystallize the melt. After about 15 minutes the temperature was raised to within 50° C. of the melting point, in preparation for the next run. A typical plot is given in figure 3. The melting point was assumed to correspond to the break in the heating curve and to the point of maximum heat absorption on the differential thermal curve. Because of the nature of these thermal effects, it was necessary to determine the points by the constructions illustrated in figure 3. The results of the two methods of obtaining the melting point usually agreed within 0°.4 C., and the value of the point of maximum heat absorption on the differential heating curve was chosen preferentially. The average of three such runs and constructions determined the base point, i.e., the thermocouple e.m.f. at which the last crystal melts at atmospheric pressure. All further runs at the various pressures for a particular setup of apparatus were referred to the base point determined in this manner. This point was assigned the value 1,391°.5 C., the accepted melting point of diopside at 1 atm. The base point having been determined, the pressure was raised to the desired value. The pressure was read at some convenient time after the heating rate had been established and again immediately after the melting point. The rise in pressure, due to the increase in temperature, was assumed to be linear between readings.

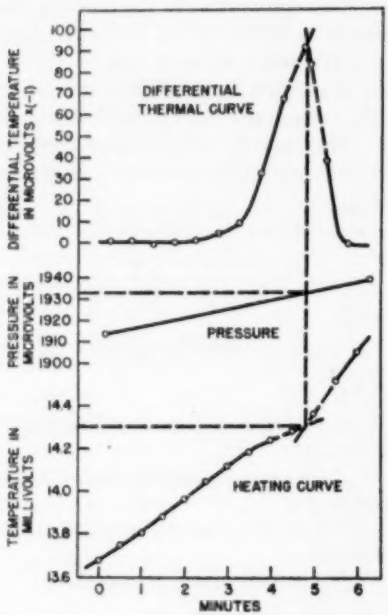

FIG. 3.—Typical plots and constructions used to determine the pressure and temperature at the melting point of diopside.

RESULTS

Five successful experimental assemblies resulted in some fifty determinations (table 1) of the melting point of diopside under pressures up to 5,000 bars. The data can be expressed by the following equation:

$$t_m = 1{,}391.5 + 0.01297P\,,$$

where t_m is the melting-point temperature in ° C. and P is the pressure in bars. The correlation coefficient is 0.998, the residual variance is 0.4 per cent, and the standard error of estimate is ±0°.8 C.; therefore, a linear relation satisfactorily accounts for the data.

The data were taken at pressure points reached by both increasing and decreasing pressure; no hysteretic effect was observed.

In the preliminary experiments, some concern arose as to the effect of the solubility of argon in the melt. If argon is soluble in the melt, the melting point

would be depressed. The linear relation of melting point versus pressure suggests either that there is no lowering of the melting point as a result of the solubility of argon in the melt or that the lowering is less than the error of measurement (±0°.8 C.) at the maximum pressure (5,000 bars). Experimental proof of this suggested relation was obtained by quenching diopside glass which was held in a gas-tight, annealed-platinum capsule from temperatures 8° C. above and 8° C. below the melting point at 5,000 bars pressure.[3] The pressure was transmitted by the collapse of the walls of the soft platinum capsule around the sample. The diopside glass, which crystallizes completely during the time necessary to raise the temperature to the desired value, melted when the temperature was above the melting point determined in the regular way and remained crystalline when the temperature was below that melting point. It is concluded that no gross bias is involved in the technique of measuring the melting point under argon.

The measured change of melting point of diopside with pressure supports the prevailing view that the melting-point curve rises indefinitely.

VOLUME CHANGE

The volume change involved in the melting of diopside can be computed from the Clapeyron equation:

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H},$$

where T is the melting-point temperature, P the pressure, ΔH the heat of melting, and ΔV the volume change. The heat of melting for diopside has been obtained by other investigators in several different ways, and the results agree rather well (see table 2). Therefore, using

$$\frac{dT}{dP} = 0.01297°/\text{bar},$$

$$\Delta H = 102 \text{ cal/gm},$$

$$\Delta T = 1{,}664°.5\,K.,$$

the volume change is found to be 0.033 cc/gm (10.8 per cent).

TABLE 1

CHANGE OF MELTING POINT OF DIOPSIDE WITH PRESSURE

P (Bars)	Δt (° C.)	P (Bars)	Δt (° C.)
285	4.5	1514	19.4
428	5.7	1514	19.8
429	5.7	1797	23.1
498	6.5	1798	23.1
498	6.5	1978	27.9
579	7.9	1986	27.4
581	7.0	2039	28.0
781	9.8	2039	26.8
781	10.2	2041	26.8
812	10.4	2585	33.0
1003	12.0	2587	33.4
1004	11.4	2590	35.4
1014	13.1	3248	42.4
1014	14.9	3250	44.0
1014	14.5	3250	42.8
1051	15.2	3722	47.7
1107	12.4	4210	53.5
1109	13.7	4212	53.9
1110	12.4	4212	54.3
1116	12.9	4622	58.0
1196	16.2	4630	60.4
1371	16.8	4987	64.9
1472	17.8	4992	64.1
1475	20.7	5010	65.8
1512	19.4		

The volume change at the melting point can be approximated by using the density of diopside, 3.275 (Allen and White, 1909, p. 14), and that of its glass, 2.846 (Larsen, 1909, p. 271), measured at room temperature.[4] On this basis the vol-

[3] This technique has been successfully used by Goranson (1938) and by the writer in the albite-water system at extreme pressures (unpublished).

[4] The determination of the density of synthetic diopside by Allen and White is incorrectly given in the *Smithsonian Physical Tables* (8th ed.) and in the *Handbook of Physical Constants*.

ume change is 0.046 cc/gm (15.1 per cent). However, Dane (1941, p. 817) accomplished the extremely difficult task of measuring the density of a synthetic diopside liquid above the melting point. Using the *computed* specific volume of the crystal at the melting point and the measured specific volume of the liquid at the melting point, he found the volume change to be 0.057 cc/gm (corrected; 18.0 per cent).

The large discrepancy between the volume change obtained by Dane and that obtained by the writer may be due to a gross bias in one of the techniques. However, assuming for the moment that both values are equally reliable, an explanation is offered for the discrepancy. As has been pointed out in a previous section, diopside may not melt at a point even under favorable circumstances. In the melting interval the volume of the system changes continuously from that of the crystal to that of the liquid. This change in volume is believed to take place in the manner illustrated in figure 4. The volume change, ΔV_b, is the bulk volume change presumably obtained by Dane. The instantaneous volume change, ΔV_i, is the thermodynamic volume change presumably obtained by the writer.[5] It is possible, then, that both volume changes are significant. The difference $\Delta V_b - \Delta V_i$ must be related to the anomalous heat capacity which obtains immediately below the melting point. And it follows that the different volume changes would be accompanied by different heats of melting. Should this be the case, it will be necessary to withhold calculation of the instantaneous volume change until an instantaneous heat of melting is available. In addition, calculations of the change of melting point with pressure, using bulk volume changes and gross heats of melting, would then be approximations. However, as there is uncertainty in the computed specific volume of the crystal at the melting point used by Dane, it is believed that 0.033 cc/gm may be a more reliable value for the volume change.

TABLE 2

HEAT OF MELTING FOR DIOPSIDE

Reference	ΔH (Cal/Gm)	Method
Tammann (1903)	93 (20° C.)	Heats of solution
Vogt (1904)	102 ± 15	Heating curve
White (1909)	106 ± 15	Heating curve
Bowen (1916)	108	Freezing point lowering
Bowen and Schairer (1929)*	97	Freezing point lowering
Kracek (1950)†	102	Heats of solution

* Computed by R. W. Goranson (1942).
† Unpublished data.

GEOLOGICAL SPECULATION

The determination of the melting point of minerals under pressure is of importance to the general problem of magma (see definition by Shand, 1950) production and extrusion. For the purpose of illustration, a brief quantitative review

[5] In the calculation of the heat of transformation from low quartz to high quartz (Yoder, 1950, p. 831) it was necessary to use the bulk volume change to obtain a result in agreement with that obtained from calorimetric methods. This additional difficulty has not been resolved.

of the mechanics of the problem will be presented. It will be obvious to geologists that most, if not all, of the following ideas are not new. Even some quantitative aspects of the argument have been presented previously in detail, principally by Kennedy and Anderson (1938), Daly (1933, pp. 66, 247–250), and Bowen (1928, pp. 314–315).[6] However, the present quantitative expression of these well-known concepts may bring new appreciation of their significance.

It is assumed that the crustal layers of the earth are entirely crystalline and under pressures equivalent to the weight of the overlying rock. Let us consider a slab of anhydrous rock composed mainly of basalt, 400 × 25 × 1 miles at a depth of 25 miles. The dT/dP for basalt is estimated to be 10°/1,000 bars, based on the previously described experimental work, with the beginning of melting taking place at 1,000° C. at 1 atm. At the base of the crust (25 miles) the temperature is assumed to be about 1,075° C.; that is, the temperature is in excess of that required for beginning of melting of the rock at 1 atm.[7]

It is conceivable that the pressure on the slab might be reduced as much as 5,000 bars, if, *for example*, gentle arching of the overlying rock took place in such a manner along the main axis of the slab that a portion of the weight would be relieved.[8] As a result of the arching process or through some other process, tensions are built up, developing fractures which are accompanied by tectonic earthquakes having shallow (20–25-mile) centers. The earthquakes themselves, which precede the great extrusions, are indicative of the release of stress but do not necessarily mean relief of hydrostatic pressure.[9]

On release of pressure the slab possesses a temperature in excess of that required for initial melting at the reduced pressure, and melting takes place. The heat of melting is probably supplied by the slab itself; that is, the melting proc-

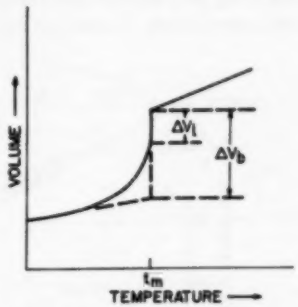

FIG. 4.—Theoretical change of volume with temperature in the region of the melting point, t_m.

[6] Note a correction in Bowen's development that 25 per cent instead of 40 per cent of the mass would be melted by the release of pressure.

[7] The assumed temperature (see Holmes, 1915; von Wolff, 1928; and Daly, 1933) is high compared to most recent estimates; however, the error is probably no greater than that involved in the temperature required for initial melting of basalt. The exact *values* are not significant; the *relation* of the geothermal gradient to the melting curve is of great significance.

[8] It has been argued by some (see Daly, 1938, p. 423) that rock does not have sufficient strength to support an arch; however, Vening Meinesz (1934, pp. 44–48) has made quantitative calculations which show that, for a multilayered crust, an arch of sizable magnitude (wave length = 62 km.) can be sustained without breaking. Even if the arch should fail, thrust faults or horst formation would, in effect, bear the load. In addition, account has not been taken of the many fold increase in strength of rocks under high confining pressures (see, e.g., the work of Griggs, 1936). The fact is that arches in the earth's crust—geanticlines—do exist.

[9] For discussion of the relation of earthquakes to volcanism, see the example of Central America presented by Sapper (1927). For other views on the relation of stress release to release of hydrostatic pressure see Graton (1945, pp. 204–205) and Daly (1943, p. 446). The earthquakes considered here are tectonic and are not to be confused with the volcanic earthquakes having very shallow (1–2-mile) centers which usually precede local eruptions in increasing frequency and magnitude (see Minakami, 1947, p. 74; 1949, p. 128).

ess is adiabatic. For example, if approximately 5,000 bars pressure are released, the slab has approximately 20° C. in excess of that required for melting (fig. 5). Since the specific heat of the hot rock is about 0.30, it has approximately 6 cal/gm available to melt a portion of the rock. The average heat of melting for silicates is probably near 100 cal/gm; therefore, some 6 per cent of the slab will melt.

The melting process involves a considerable volume change. Assuming the rock

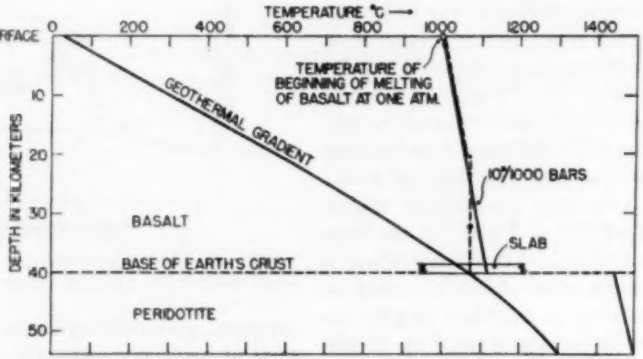

FIG. 5.—Relationship of geothermal gradient to beginning of melting curve of basalt (*solid curves*) and temperature change with pressure (*dashed curve*) of a hypothetical magma produced and extruded in the manner described in the text.

density is 2.95 and the density of its liquid is 2.65 at the high temperature, the volume change on melting is 11.2 per cent. Because 6 per cent of the volume of the original slab is 600 cubic miles, the increase in volume due to melting is about 70 cubic miles. The space for this increase in volume may be obtained (1) by further arching of the superincumbent rock or (2) by some of the magma rising in the fractures developed upon relief of stress. Consider the second possibility: the 70 cubic miles of mobile molten rock can fill a channel 150 miles long and 100 feet wide from the bottom of the crust (25 miles) to the surface. Reflecting on the size of the average volcanic channel, the conduit would be filled to overflowing.[10] No matter how a magma is produced from crystalline material—by heat from a local hot spot, by relief of pressure, by actual unloading, by lowering of the melting point through stress—the considerable volume change must be reckoned with.

The molten portion may collect and rise in the fractures; however, it is more likely that the mobile liquid + crystal mush will rise in bulk. The composition of the mobile mass will be quite different in the two cases. In rising, the pressure is further reduced, more melting takes place, and the ratio of liquid to crystals increases. Yet it is a rare occurrence when a basaltic magma reaches the surface in an entirely liquid condition. Furthermore, the outwelling of lava may be continuous or discontinuous and may extend over thousands of years.

[10] Dr. E. G. Zies suggests that this particular phase of the mechanism be epitomized by the term "swelling hypothesis." Apparently Verhoogen (1946, p. 761) also had this idea in mind.

It is assumed that the magma retains most of its heat, although both exothermic and endothermic reactions are taking place. Little heat will be lost to the walls in transit because of the low thermal conductivity of hot rock and its small heat capacity. Because in the assumed mechanism a free path is provided to the surface, assimilation (which requires large amounts of heat, 100 cal/gm) is probably negligible. It is obvious that in this particular process the magma cannot possess superheat. The fact that some inclusions, which have been observed to be few in number in basalts, are only slightly altered may indicate that (1) insufficient time was available to digest the inclusion or that (2), in consequence of the loss of heat in the digestion process, the magma crystallizes.

If the heat losses are excessive, the magma begins to crystallize as it rises. The composition of the initial liquid shifts with decreasing pressure toward those minerals having the larger partial volume change (for illustration of principle, see fig. 6). It would be expected, then, in the feldspars, for example, that at high pressures the first-formed plagioclase would be slightly richer in anorthite than the first-formed plagioclase at a lower pressure in rock-forming liquid systems.[11]

It should be clear that the individual volcano is of minor importance compared to the magnitude of the system; it is only one of the many chance openings on a long compound fracture. The linearity of the great volcanic mountain chains attests to fracture control, and the great basaltic lava flows, where studied (see list of important fissure eruptions compiled by Daly, 1933, p. 264), have poured out of long simple and compound fractures.

The mechanism for the production and extrusion of a magma (nonexplosive type) which has been presented follows in a general way the epigram "Diastrophism is the mother of volcanism." As in most cases the investigator tends to emphasize that with which he is most familiar; nevertheless, it is hoped that the above quantitative presentation of well-known ideas will bring greater appreciation of the need for data on the melting of rock-forming minerals under pressure, their volume changes on melting, and their heats of melting.

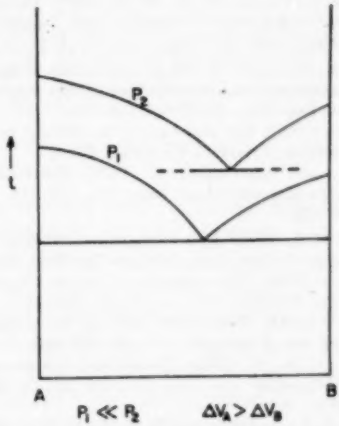

FIG. 6.—Change of liquidus temperatures with pressure of a simple binary system.

The role played by the volatiles, especially important in those magmas which exhibit dynamic phenomena in the upper part of the lava column, has been neglected in the foregoing discussion. It is anticipated that on the completion of the work under way on the diopside-water system, the effect of volatiles on a basaltic magma may be deduced in a similar quantitative way.

[11] It is of passing interest to note that, at approximately 22,000 bars pressure, albite and anorthite would melt at the same temperature!

ACKNOWLEDGMENTS.—Much of the success of the high-pressure and high-temperature experiments is the result of the skilful construction and assembly of the apparatus by Mr. John Van den Heurk. The generous contribution of his free time and effort is very gratefully acknowledged. Discussions with Drs. L. H. Adams, N. L. Bowen, F. Chayes, J. W. Greig, and E. G. Zies were very helpful in preparing the manuscript.

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ARROYO-CUTTING AND FILLING[1]

ERNST ANTEVS
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ABSTRACT

Arroyos are the vertical-walled, flat-floored channels of ephemeral streams of the semiarid Southwest formed both since 1880 and during some past ages. Arroyo-cutting takes place because the plant and soil mantle is poor or destroyed and permits the water of violent showers to run off too fast and form torrents in trails, ruts, ditches, and stream beds. Filling occurs when the runoff is slowed by vegetation so that it drops its load. Thus both cutting and filling are controlled mainly by the condition of the plant cover, whose natural control, in turn, was moisture. Vegetation was poor, and channeling took place during droughts, filling occurred during climatic transitions, and soil formation during relatively moist ages. The modern impairment of the vegetation coincided with a great increase in livestock and is a consequence of overgrazing and human activities. It is not a result of drought, for the primeval vegetation still remains or has recovered in areas protected from livestock.

Arroyo-cutting was caused mainly by drought in the past and by overgrazing since 1875. Past arroyo-filling was caused by a moderate moisture increase.

INTRODUCTION

The word "arroyo" was used by Kirk Bryan in 1925 for the channels which have been cut since about 1880 in the southwestern United States. These trenches have flat floors and vertical banks. They are of all sizes up to 100 feet deep, many hundreds of feet wide, and 140 miles long. They are incised in unconsolidated materials consisting of clay, silt, sand, and some gravel. They are dry or have only a trickle of water except during rains and snowmelt; their streams are thus mostly ephemeral. These channels occur in Arizona and New Mexico and in contiguous parts of California, Nevada, Utah, Colorado, Texas, and Old Mexico. They are essentially confined to semiarid regions (Thornthwaite, 1948, pl. 1). They were cut, according to most scientists who have studied them, by occasional flash floods after the vegetation had been severely reduced.

The distinctive features make it appropriate to reserve the word "arroyo" as a geomorphic term for these and identical channels, old and buried as well as modern. Desert washes, or wadis, which also are flat-floored and steep-walled, differ by being eroded mainly in gravel and independently of vegetation. The flat-bottomed, steep-walled trenches, dry most of the time, which occur in many minor valleys in central and southern United States, are strikingly similar to arroyos (Happ, Rittenhouse, and Dobson, 1940, pp. 16, 17, 52, 78, 79, 106, pls. 3, 11*B*, 16*B*), and their formation "has been accelerated by human cultural influences including deforestation, cultivation, and grazing" (Happ, 1948, p. 1213). They differ, however, in other respects. They occur in moist climates. They are limited to the headwater parts of valleys and are consequently also limited in size, especially in length. Near Oxford in north-central Mississippi, they attain a depth of 12 feet, a width of 50 feet, and a length of over ½ mile. They are flumes which "transport sediment from the gullied and sheet-washed uplands past the upper parts of the flood plains, where much deposition would

[1]Manuscript received June 1, 1951.

otherwise occur, to the wider valley bottoms farther downstream" (Happ, Rittenhouse, and Dobson, 1940, pp. 16–17).

There have been several attempts to explain modern arroyo-cutting and some endeavors to account for the past channeling and filling. The principal suggested causes of *modern* trenching are as follows:

1. Overgrazing, trampling, and human activities, which reduced or destroyed the vegetative cover and made trails, ruts, and ditches, which, in turn, led to greatly accelerated and concentrated runoff, resulting in violently erosive flash floods after torrential rains (Thornber, 1910, pp. 336–339; Rich, 1911, pp. 241, 242; Bailey, 1935, p. 355; Antevs, 1941, p. 37; Thornthwaite, Sharpe, and Dosch, 1942, pp. 127, 128; Cottam, 1947, pp. 18, 24, 26; Happ, 1948, pp. 1192, 1213).

2. Increase in moisture, which induced denser vegetation, and longer, steadier, and clearer streams with considerable erosive power in the valleys. Grazing, trails, and ditches "simply served as the means, so to speak, of pulling the trigger which allowed certain natural forces to come into play" (Huntington, 1914, pp. 32–35). Huntington did not attribute the channeling to "a slight change of climate toward dryer conditions," as Bryan (1925*b*, p. 343) has stated. Huntington's views do not hold for the Santa Cruz River in southern Arizona, to which he applied them, or for arroyos in general, because of the extraordinary erosive and transporting power of occasional flash floods. The heavy floods which in 1889 and 1890 started the arroyo at Tucson did not introduce a moist age, for in 1891 and 1892 the rainfall was again below the average.

3. "Sudden violent showers followed by unobstructed runoff," together with grazing and forest-cutting (Gregory, 1917, pp. 131, 132).

4. Increasing dryness of climate, which reduced the vegetation and promoted the runoff, which, in turn, enlarged the magnitude and the erosive and transporting power of floods. "Overgrazing should be regarded as a mere trigger pull which timed a change [of climate] about to take place" (Bryan, 1928*a*, pp. 279–281; see also Bryan, 1925*b*, p. 343; 1941, pp. 232–236; 1950, p. 121; Hack, 1942, p. 67).

The assumed causes of *past* arroyo erosion are:

1. Drought which severely depleted the vegetal cover and thereby so facilitated runoff that occasional cloudbursts caused raging floods (Bryan, 1928*a*, p. 281; Antevs, 1941, p. 38; Hack, 1942, p. 67).

2. "Vicissitude within a climatic epicycle" (Bailey, 1935, p. 355), "irregular occurrence of heavy storms rather than in any change of climate," or intense storms and "heavy fall of precipitation rather than a general climatic trend" (Thornthwaite, Sharpe, and Dosch, 1942, pp. 89, 124, 126). This view resembles that of Gregory for modern trenching.

The proposed causes of arroyo-filling, temporary or permanent, are:

1. Increasing dryness or drought, which reduces the vegetation so that the streams will be heavily loaded and aggrade their valleys "so long as aridity continues" (Huntington, 1914, pp. 31–34).

2. "Low water" and absence of large floods, but "cyclic conditions of aridity" are not implied (Gregory, 1917, p. 132; Smith, 1938, pp. 49, 50; probably Thornthwaite, Sharpe, and Dosch, 1942, p. 89).

3. "A slight change from the dry towards the less dry in climate," which improves the plant cover so that floods are reduced and slowed until they drop their mud loads (Bryan, 1941, p. 236; see also Albritton and Bryan, 1939, p. 1472; Hack, 1942, p. 67; Antevs, 1949, p. 52).

The immediate controlling factor of both arroyo-cutting and arroyo-filling may be the condition of the vegetal mat; this, in turn, may have been determined in the past by moisture conditions and, since about 1875, mainly by livestock and man. To test this thesis, I shall examine and review the relationship between the state of the plant cover and geological processes, the unspoiled natural conditions and their destruction, modern arroyo erosion, and the exposed valley sediments and their conditions of formation.

Knowledge of the real causes of past and present channelings is of both economic and scientific importance. Such knowledge is necessary to judge whether or not, and by what means, the modern trenching can be checked; the channels filled; and the land, vegetation, and water table reclaimed and restored. If ancient channeling and filling were results of climatic changes, then how pronounced were these, when did they occur? How old are the artifacts and other records of man buried in the fills?

GENERAL ROLE OF PLANT COVER

A cover of live vegetation and of porous plant litter possesses a remarkable ability to bind the soil, to retain the water of rains, and to keep it free from mud. The associated humus-rich and porous topsoil serves as a sponge (U.S. Dept. Agriculture, 1938, pp. 595, 609, 610, 620–623). The effectiveness of vegetation, plant litter, and topsoil in neutralizing heavy rains is well illustrated in Utah and Idaho. Here are found vegetated slopes as steep as 60°, whereas bare talus slopes are generally less than 35° (Bailey, 1941, p. 241). Beneath the vegetation and litter are fine-grained soils. "The plant cover is the key to stability." Observations, measurements, and history "amply justify the conclusions that many watersheds in the semiarid West may develop a sufficiently complete plant-and-soil mantle to allow an infiltration rate equal to the greatest magnitude and intensity of storms" (Bailey, 1941, p. 248).

In contrast, a poor or badly impaired mantle of vegetation and soil sheds most of the water of hard showers even on gentle slopes, because the runoff is almost unobstructed and because a bare ground surface is fairly waterproofed by splash and mud. The impact of the raindrops destroys the loose structure of the soil and compacts it to an almost impervious paste, and colloidal mud enters and seals pores and cracks (Ellison, 1950, p. 247). As a consequence, the rainwater rushes downhill, washes away soils, and gathers into torrents or flash floods, channeling the valley floor or stream bed. An observation by Ives (1936, p. 354) in the Sonoyta Valley, northwestern Sonora, is instructive. About half an hour after a summer noon rain had begun in the Sierra de Cubabi, streams of water came roaring out of gullies in the granite and spread into a sheet flood over the alluvial cones. The front of the water sheet was about 3 inches high, and after a few minutes the water was 1 foot deep. The waters raised the Sonoyta River in forty minutes from a depth of 1 foot to a depth of 30 feet. Next morning the river had dropped to a depth of 10 feet. The flood cut a new gash in the Sierra, a gulch

50 feet wide and deep and 1,000 feet long.

North of Salt Lake City, extraordinary, destructive floods have originated in areas with recently depleted vegetation and soil, whereas no damaging runoff arose from adjacent and interspersed well-vegetated areas which must have received the same amount of rainfall (Bailey, 1941, p. 245).

VIRGIN VEGETATION AND STREAMS

Observations made on the vegetation in Arizona and New Mexico during 1843–1881 by army officers and others have been gleaned from their reports and diaries by Bryan (1928*b*), Thornthwaite, Sharpe, and Dosch (1942, pp. 65–68), and Leopold (1951). Similar observations in Utah by explorers and Mormon pioneers have been collected by Stewart (1941) and Cottam (1947, pp. 9–12). Those relating to the Southwest show that there were large expanses of grassland in southeastern Arizona (Leopold, 1951, pp. 295, 307–310), southwestern New Mexico (p. 308), and the Little Colorado drainage of northeastern Arizona (pp. 305–307). The grazing was relatively poor in the Rio Grande Valley of northern New Mexico except in well-watered bottom lands (pp. 300, 307). The grass cover was good in some reaches of the Rio Puerco in New Mexico, although it was poor in others (pp. 295, 305). It was no longer primeval but was depleted by overgrazing near Las Vegas, Santa Fe, and several Indian villages (pp. 299, 300, 305, 306; Thornthwaite, Sharpe, and Dosch, 1942, pp. 65–67). In Utah "grass was originally an important and conspicuous element of the foothill vegetation" (Cottam, 1947, pp. 9, 12). In some places it formed pure grasslands, in others it was associated with shrubs. At present these vast uplands are dominated by sagebrush, rabbitbrush, and shadscale.

The unspoiled natural conditions in southeastern Arizona have been described by Thornber (1910, p. 334), a botanist who began to study the Arizona grazing ranges in 1901. He states that before there were large herds of livestock—that is, before 1880—the country had a fairly continuous plant cover of many kinds of grasses and other forage plants. The centers of the valleys were in part covered by dense carpets of tall sacaton grass, forming wet meadows (cienegas). Elsewhere in the valleys the water table was commonly within a few feet of the surface. There were cottonwoods and thickets of catclaw and mesquite. The surface runoff was small, for the rainwater percolated into the ground. Thus slowly fed, many more streams were permanent than now, and large floods were rare. Small streams had poorly defined channels.

The reported poor stands of grass in some places might have various causes. Unsuitable soils may have been a factor in some areas; the climate may have been too dry in others; and, as mentioned, overgrazing was the cause in still other places. It is noteworthy that, although the Navajo Indians did not possess large herds of sheep until 1868, their habit of bringing the animals to corral each night led to destruction of the plant mat in the surrounding area (Thornthwaite, Sharpe, and Dosch, 1942, pp. 69, 71, 122). Under natural conditions a century ago poor or impaired vegetation was rare in the valleys in which arroyos later were cut. The view of Thornthwaite and associates (1942, pp. 111, 127), that the vegetal cover in many places of such valleys was poor and delicately adjusted to climate, is an exaggeration.

The Whitewater Draw near Douglas in southeastern Arizona was originally intermittent and was a shallow, hardly noticeable depression, partly grass-covered, which here and there expanded to mud flats and pools (Meinzer, 1913, pp. 11, 28). The deposit formed between 1300 and 1880 is a yellow-white, faintly laminated silt or sandy silt, commonly about 1 foot thick (Antevs, 1941, p. 43). The stream is now ephemeral.

The Santa Cruz River at Tucson had an insignificant channel and was bordered by a grass-covered plain a mile wide, over which floodwater moved slowly without causing any erosion (Huntington, 1914, pp. 24, 33; Bryan, 1922, p. 77). I do not know the nature of the flow in the 1880's, but about 1700 this was probably perennial (Bryan, 1922, p. 78). At present the flow at Tucson is ephemeral (Schwalen, 1942, p. 454). About 10 miles south of Tucson the top sediments are yellow silt and incipient silty soil.

On the Colorado Plateau the valley centers, judging from now exposed sediments, were occupied by braided streams and locally by meadows, swamps, and ponds (Bailey, 1935, p. 340).

Gullies were reported by explorers before the general, deeper, and longer channeling started during the 1880's. Thus Rio Puerco, west of Albuquerque, New Mexico, in 1846–1877 locally occupied trenches that were up to 30 feet deep and 100 feet wide, whereas at other places it had inconspicuous banks (Bryan, 1928*a*, pp. 268–279; Leopold, 1951, pp. 301–305). Chaco River in northwestern New Mexico had had an arroyo since about 1860. In 1877 this was 16 feet deep and 60 feet wide at one place (Bryan, 1925*b*, p. 340; 1941, p. 229). The Polacca drainage had discontinuous channels (Thornthwaite, Sharpe, and Dosch, 1942, p. 105). There were early gullies also in the Rio Grande Valley, near the Arizona–New Mexico state line west of Gallup, west of Holbrook, and near Tucson and Benson (Leopold, 1951, pp. 300, 305–310).

A few of these gullies were probably desert washes rather than arroyos. Some were surely consequences of local overgrazing and man's activities. Those of the Rio Puerco were dependent on the entrance of large tributaries and on narrowness of the valley floor (Bryan, 1928*a*, p. 279).

DEVASTATION OF THE VIRGIN VEGETATION AND DATE, PLACE, AND RATE OF MODERN ARROYO-CUTTING

The destruction of the primeval vegetation and its consequences are well illustrated in southeastern Arizona and vividly described by Thornber (1910). During the Spanish occupation there were several large haciendas in the region, but during the 1820's the Apache Indians broke up the settlements and scattered the herds (Darrow, 1944, p. 313). Cattle were reintroduced in the early 1870's by Anglo-Americans. Except for raids by the Apaches, the country was rendered very attractive by the abundance of water and forage and by the mild winters. The number of livestock increased rapidly (Thornber, 1910, pp. 335, 338). "Since the country was practically all public domain, each man was free to graze as much stock on it as he was able to possess, without restriction, and without any consideration as to the carrying capacity of the grazing areas . . . . That which was free for all to use came to be regarded as free for all to despoil" (p. 336).

"This overstocking soon resulted in destructive overgrazing and trampling out of large areas of forage producing

plants, often beyond recovery" (p. 337). As a consequence, the rainwater raced down slopes and trails. "Once in the cienegas and rivers, these accumulated waters developed into most destructive floods, cutting in the rich alluvial soils of these formerly well-watered valleys, within the space of a remarkably few years, permanent channels 5 to 30 feet deep, and 50 to 300 feet wide" (p. 338). It is thus a matter of record that the grazing ranges were denuded by excessive numbers of livestock and that this despoliation was accompanied and followed by arroyo-cutting.

Thus arroyo-cutting began in 1885 in the heavily grazed Sulphur Spring Valley, and by 1910 the Whitewater arroyo was almost as long, deep, and wide as it is now (Meinzer, 1913, p. 28; Antevs, 1941, p. 31). The channel begins about 20 miles below the headwaters and extends for the next 20 miles to the Mexican border and probably beyond. It averages 13 feet deep and 100 feet wide.

Channeling by the Santa Cruz River was started in 1889 by exceptionally heavy floods after the vegetation had been reduced by cattle and the flood plain transected by trails and irrigation ditches (Huntington, 1914, pp. 33, 34). The first gullies were formed along ditches in the vicinity of Tucson and were extended rapidly upstream and downstream. Now the arroyo reaches from a point 15–20 miles below the headwaters for 120 miles to Rillito, 15 miles northwest of Tucson (Schwalen, 1942, pp. 422, 424, 427). It is in places as much as 25 feet deep and several hundred feet wide. In its uppermost course the Santa Cruz occupies a small channel floored by sand and gravel and has a small permanent flow.

The large majority of the arroyos in the Southwest began forming during the 1880's (Bryan, 1925*b*; Thornthwaite, Sharpe, and Dosch, 1942, pp. 102–104), but, as stated, several discontinuous gullies started earlier. Arroyos occur in the upper reaches but rarely in the headwaters (Antevs, 1949). The bulk of the dislodged material is deposited in the distal part of the channel, below the arroyo terminus, or farther downstream. The debris from the Santa Cruz arroyo forms a fan with its handle at Rillito. Floodwaters follow shifting courses over this fan. They rarely reach Gila River, 95 miles northwest of Rillito.

Arroyo erosion is incredibly rapid until a channel has been formed which can accommodate the big floods. A gully 60 feet deep and 15 miles long was cut by Kanab Creek, Utah, in three years, 1883–1885 (Gregory, 1917, p. 131). The channel of the San Pedro River was extended for 125 miles in ten years, 1883–1892 (Bryan, 1925*b*, p. 342).

BEDS EXPOSED IN THE MODERN ARROYO WALLS AND THEIR CONDITIONS OF DEPOSITION

The beds exposed in the walls of the Whitewater arroyo consist of clay, soil, silt, sand, and fine to cobbly gravel, with clay as the main constituent. The fine-grained materials, including soils washed from uplands, are commonly mixed in various proportions. The deposits are well bedded in most places, and some are laminated. Some beds were eroded, others were changed by soil-forming processes (Antevs, 1941).

The strata dissected by the Santa Cruz arroyo, about 10 miles south of Tucson, also range from clay to gravel. Silt forms the bulk, whereas gravel is of small amount. Typical exposures show silt beds, 0.5–8 feet thick, alternating with incipient silty and clayey soils from 3 inches to 3 feet thick. Some sections

show as many as thirteen soils and humus-stained zones. Thin layers rapidly peter out.

On the Colorado Plateau the valley fill is largely sand, with considerable clay and a little gravel. The sands are well stratified, laminated, and cross-bedded. There are also incipient soils and thin peat layers (Bailey, 1935, p. 340).

The mode and conditions of formation of the various kinds of deposits may be observed at present or judged from known virgin conditions. Gravels and some sand deposits are residues left on the arroyo floor during ages of channeling. During years of only small and moderate floods, debris of various coarseness accumulates in the arroyo, especially if this is very long, where the current is reduced by low gradient, vegetation, meanders, or absorption of the water by the dry stream bed. This has made some students attribute arroyo-filling to low water or drought, as noted previously. However, such deposits are for the most part only temporary. The fine-textured debris, especially, will be swept farther or out of the channel, by the next large flash flood, such as those of the Santa Cruz during the winters of 1904–1905 and 1914–1915 and during January, 1916 (Huntington, 1914, p. 34; Smith, 1938, pp. 49, 50; Schwalen, 1942, pp. 457, 463). Only a small part, mostly gravel, will remain in places. Therefore, buried gravels and some sands (Thornthwaite, Sharpe, and Dosch, 1942, p. 86) signify old arroyos. They clearly do so when gravels and sands occur on the floor of an old filled channel exposed in a modern arroyo wall.

One kind of clay deposit, though negligible in amount, is important. Arroyo floors commonly have depressions, perhaps 20 by 50 feet and 5 feet deep. Those cut in clayey beds hold muddy water, in some cases for weeks, after an arroyo run and serve as water holes for livestock and wildlife. Such tanks are termed "charcos" by Bryan (1925*a*, p. 121). As the water evaporates, a clay film is deposited. In the past, Paleo-Indians camped at charcos and left artifacts, broken animal bones, and charcoal from fires in the clay. In geologic-climatic dating it is important to recognize these fine-grained charco clays and to assign them to ages of trenching.

Sand and gravelly sand were deposited in stream beds and on floodplains. Most silt was laid down on mud flats and on well-vegetated floodplains. Soil, eroded from uplands, and clay were laid down by sheet floods moving over grass-covered gentle slopes and by stream floods on floodplains with good vegetation. Laminated silts and clays were deposited in relatively permanent lakelets, probably dammed by beavers (Antevs, 1941, pp. 34, 35). The humus-stained zones and soils exposed in arroyo walls formed slowly where and when there was vegetation and no significant accumulation or erosion. Most of them thus developed on relatively high parts of floodplains during ages of small floods and/or of clear waters; but some humus-stained zones probably formed on any part of a former floodplain that fulfilled the stated conditions when floods were confined to an arroyo.

CONDITION OF THE PLANT COVER THE IMMEDIATE CONTROLLING FACTOR

As noted, a good and healthy plant cover and soil mantle will, with rare exceptions, prevent arroyo-cutting by torrential rains; a poor or impaired vegetation and soil will permit such erosion. The primeval vegetation in the semiarid regions of the Southwest was almost uni-

versally fair, good, or ample. As a consequence, there was generally deposition or soil formation in valleys and on floodplains, rarely natural channeling. The native grazing ranges were denuded in one to a few decades after the introduction of livestock in large numbers, and a general arroyo-cutting followed promptly.

Of the deposits exposed in the arroyo walls, gravels, some sands, and charco clays, together with filled channels, indicate past ages of flash floods and accelerated runoff, which, in turn, signify poor plant covers both in valleys and on uplands. Most clays and silts and some sands suggest considerable surface runoff and erosion on the uplands and signify sparse to fair vegetation on uplands, fair to good in valleys. Soils and most humus-stained zones imply good to ample vegetation on uplands as well as in valleys.

TABLE 1

RELATIONSHIP OF MOISTURE, VEGETATION, AND GEOLOGICAL PROCESSES

Climate	Plant Cover	Process
Dry	Impaired or poor	Accelerated erosion, arroyo-cutting leaving coarse residue)
Intermediate	Sparse to fair on uplands; fair to good in valleys	Deposition
Relatively moist	Good to ample	Neither erosion nor deposition; soil formation

In brief, the state of the vegetative cover is the immediate controlling factor of arroyo-cutting and filling and of soil formation on floodplains in the semiarid Southwest.

The view of Thornthwaite and associates (1942, pp. 89, 124) that heavy storms were the main controlling factor stemmed from their belief (pp. 111, 127) that the primeval vegetation was poor and delicately adjusted in many places in later channeled valleys. Their evidence of destructive rains (pp. 112–119) has only moderate weight, because in most places vegetation and land had already been reduced and disturbed by livestock, man, accelerated runoff, gullying, and lowering of the water table. Also, if torrential rains had been really decisive, there should have been many more discontinuous gullies in the 1870's, and there should be numerous channels of all ages in the arroyo walls. But, in spite of diligent search by geologists and archeologists, only a small number of buried arroyos have been found, the youngest, dated by potsherds in its fill, cut during the drought of A.D. 1276–1299.

ULTIMATE CAUSES

The real causes of arroyo-cutting and filling in the semiarid Southwest are consequently the factors which determine the controlling conditions of the vegetal cover. The ultimate controlling factor of the plant mat, before there were large herds of livestock, was moisture; and the density of the vegetation was roughly proportional to the moisture. Indian farming seems to have had little or no influence (Thornthwaite, Sharpe, and Dosch, 1942, p. 107). The probable causal connection between moisture, vegetation, and geological processes is shown in table 1.

Thus natural arroyo-cutting takes place during droughts; arroyo-filling and floodplain aggradation during transitions of the moisture conditions. Buried soils derive from relatively moist ages; but some humus-stained zones probably date from dry ages, having formed in

favorable sites on abandoned floodplains when floods were confined to channels.

These conclusions, however, are opposed by the view of Thornthwaite, Sharpe, and Dosch (1942, pp. 45, 88, 89, 123, 125, 127) that all old arroyos in the Southwest were cut and filled not as results of distinct climatic changes but under "normal" or "natural" climatic conditions, which include "climatic fluctuations of the magnitude experienced today." They believe that the channels were eroded by floods during occasional intense storms and that the material was carried a short distance down-valley and deposited as fans filling the distal ends after the trenches had attained some length. The view is closely associated with their belief (pp. 111, 127) in a delicate adjustment of vegetation to climate and is partly founded on an overrating of the role of rains and an underrating of the vegetative cover and its protective competence. Because the writers particularly refer to Hack's (1942) study of several valleys adjacent to their Polacca Wash and as the oldest fill distinguished by Hack contains remains of elephant, their "normal" climate in this discussion must comprise the climates during the last cool-moist pluvial and ever since, including the warm-dry Altithermal (Antevs, 1948). Obviously, they here gave "normal" entirely too wide a range, a fact they seem to have sensed when writing the summary, in which (p. 125) they refer only to the last two thousand years. The view is thus also based on unfamiliarity with the amplitude of the climatic changes during the last ten thousand years. Therefore, our conclusions in the preceding paragraph seem justified.

The modern impairment of the vegetation, which began in most regions during the 1870's, is a separate matter. It coincided with a great increase in livestock and in human activities, with overgrazing and other despoliation. Still, to Bryan (1950, p. 121; 1928*a*, p. 281), "overgrazing appears to have been merely a trigger pull which timed the explosive process that was imminent from climatic causes." In support of Bryan's view, Hack (1942, p. 67) quotes Schulman's tree-ring studies.

The precipitation in New Mexico during 1850–1870 underwent considerable fluctuation, and the average was somewhat above that of the last hundred years. The rainfall in Arizona and New Mexico in the period 1871–1904 was, on the whole, below the mean, though locally well above the average during certain years, especially in 1881, 1884, and 1897. The state unit rainfall (U.S. Dept. Agriculture, 1941, pp. 765, 1017) was generally below the average from 1886 (the first year a figure is available) to 1904, especially in Arizona. The state unit values were, on the whole, above the mean in Arizona during 1905–1923 and in New Mexico during 1905–1932. The tree growth in dry situations at the lower, dry limit of timber in the Southwest records substantially the same moisture history (Schulman, 1942, pp. 213, 215; 1946, pp. 41, 45). The growth was mostly above the average in 1850–1870; below the mean, except for secondary maxima, in 1871–1904; and generally above the average from 1905 to 1920, 1928, or 1930.

If the subnormal precipitation in 1871–1904 had been the principal cause of the impairment of the vegetal cover which led to the general arroyo-cutting, then the above-normal rainfall from 1905 to 1923 or 1932 should have distinctly improved or restored the plant cover. But this it did not do. On the other hand, protection from livestock

grazing and trampling enabled the vegetation on the grounds of the Desert Laboratory at Tucson, moderately grazed before 1907, to make a remarkable recovery during the years 1906–1936 (Shreve and Hinckley, 1937, pp. 463, 464, 478). Though the rainfall at Tucson during the eight years 1928–1936 averaged only the mean value, the increase in density of the plant cover was then much greater than during the preceding twenty-two years (1906–1928), a fact "manifestly due to the slowness with which proper conditions are built up for the successful establishment of larger numbers of young plants." In Utah protected or moderately grazed areas, chiefly unused parts of old cemeteries, still support a good primeval cover of plants palatable to livestock (Pickford, 1932; Stewart, 1941, pp. 365, 373; Cottam, 1947, p. 12). Droughts since 1870 have not greatly reduced the density of forage plants here.

Clearly, if left alone, the native vegetation could have weathered the droughts during which the arroyo erosion set in during the 1880's. The impoverishment of the plant cover which permitted the channeling must have been caused by new and foreign detrimental agencies, and the new factors during the 1870's and 1880's were large herds of cattle and sheep and numerous settlers. Therefore, the reduction of the vegetal cover which allowed arroyo-cutting to begin during the 1880's in the Southwest was caused by livestock and man, the view generally held by ecologists and conservationists.

The condition of the damaged plant mat was worsened by the secondary effects, especially the accelerated runoff and the drastic lowering of the groundwater table which accompanied the deep trenching of the valley floors. As the moisture supply dwindled with the prolongation of acute droughts, such as those in Arizona about 1900 and 1950, the subnormal precipitation also contributed to the thinning of the already much reduced vegetation. Scant rainfall was a late factor in a chain reaction set off by overgrazing; but the late dry spells alone—without the detrimental effects of livestock and white man—might not have been sufficiently severe to cause a general channeling.

The main ultimate causes of arroyo-cutting in the Southwest were drought in the past and overgrazing since about 1875. The cause of past arroyo-filling was a moderate increase in moisture.

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THE STABILITY RELATIONS OF ANORTHITE AND ITS HEXAGONAL POLYMORPH IN THE SYSTEM $CaAl_2Si_2O_8$-H_2O[1]

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ABSTRACT

Hydrothermal experimentation indicates that pure anorthite is stable in the presence of H_2O at temperatures down to 350° C. and possibly lower. A hexagonal polymorph of anorthite unknown in nature is consistently synthesized at low temperatures, and the possibility of its being stable below approximately 300° C. is discussed. The hydrous phases zoisite and lawsonite were not encountered.

INTRODUCTION

The behavior of the plagioclase feldspars at low temperatures, particularly in a hydrous environment, is of considerable importance to petrology. Water is generally considered to play an important role in many later-stage igneous processes as well as in metamorphism and weathering. Hydrous minerals may be formed directly in place of a plagioclase in low-grade "constructive" metamorphic processes or as breakdown products of plagioclase during katamorphism or weathering. It is also the accepted view that the stability of the plagioclases decreases with increasing anorthite content at low temperatures in the presence of water (see Graham, 1949). Albitic plagioclase is commonly found to persist in rocks under these conditions, whereas more lime-rich plagioclase is destroyed. Zoned or cored plagioclases with an altered core and fresh exterior portion are common in igneous rocks, the interpretation being that the more sodic feldspar is stable under the conditions that produced alteration in the more calcic portions of the crystal. Saussuritization is a loosely defined process, but most petrologists would agree that calcic plagioclase is broken down to a mixture containing zoisite with or without varying amounts of calcite, sericite, chlorite, and albite or albitic feldspar. The albite, when present, was reconstituted from an unstable plagioclase. Saussuritization is a very common process, particularly in gabbroic rocks. The survival of alkali feldspars in sedimentary rocks and the destruction of calcic plagioclase by weathering are indicative of the greater stability of albite under these conditions (see Goldich, 1938). In addition, authigenic feldspars appear to be limited to the potash and soda varieties; lime-containing plagioclase does not appear to form in these lowest-temperature occurrences. It must be remembered, however, that the minerals that form in these processes of hydrothermal change, weathering, etc., commonly do so in a complex chemical system; a variety of phases can be formed, owing to the relatively large number of chemical components that may be present, whereas in a simple system the stability range of fewer minerals may be considerably extended.

Of the minerals generally considered to be formed at the expense of calcic plagioclases, zoisite and lawsonite are the closest in chemical composition to anorthite. Zoisite, $Ca_2Al_3(OH)Si_3O_{12}$, the iron-free member of the epidote series, is commonly observed to be secondarily formed

[1] Manuscript received March 27, 1952.

from plagioclase. Lawsonite, $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$, is a relatively rare mineral, but in certain of its occurrences it also is a product of plagioclase hydration and breakdown (Dana, 1932). The composition of lawsonite can be represented as precisely that of anorthite, plus $2H_2O$, and zoisite as 3 moles of anorthite plus 1 of $Ca(OH)_2$. Basing his work on combined theoretical and field studies, Ramberg (1944) has treated the plagioclase-zoisite association from an equilibrium viewpoint, considering zoisite (epidote) as the low-temperature (hydrous) equivalent of anorthite.[2] A hypothetical equilibrium diagram was drawn so that the curve separating the low-temperature field of zoisite from the high-temperature field of plagioclase falls continuously with temperature from pure anorthite to pure albite, the latter being stable under all conditions observed. The lower the anorthite content of the plagioclase, the lower the temperature at which plagioclase and zoisite coexist; this is equivalent to saying that the more albitic the plagioclase is, the more stable it is under low-temperature hydrothermal conditions.

The present investigation is a first step in the attempt to evaluate experimentally the hydrothermal stability relations of the plagioclases. The plagioclase series, plus water, is a restricted portion of the 5-component system Na_2O-CaO-Al_2O_3-SiO_2-H_2O. The present study is limited to pure anorthite plus water and may be represented as the join $CaAl_2Si_2O_8$-H_2O within the quaternary system of oxides. Because of the time-consuming nature and the unexpected results of the experiments, the data on pure anorthite are here presented; the general plagioclase relations will be communicated at a later date.

[2] It is not intended to go into detail here on the problems of zoisite and epidote, including those encountered in attempted synthesis. This will be the subject of a forthcoming paper by E. Ehlers.

EXPERIMENTAL METHODS

The experimental runs were made in two types of apparatus: 18-ml. modified Morey-type bombs and a hydrothermal quenching apparatus designed by Tuttle (1948). The various starting materials used were powdered glass of the composition of anorthite, or a mixture of $Al_2O_3 \cdot xH_2O$, SiO_2 glass, and $Ca(OH)_2$ in the proper proportions, or crystalline materials such as natural anorthite and others to be described presently. The natural anorthite used was crushed from selected clear crystals from Miakejima, Japan, and was determined to be approximately 97 per cent An by optical and spectrographic analysis.[3] The charges, of approximately 10 mg., were packed in spun platinum-foil containers and capped with slightly larger but similar spun-foil covers, the two parts, with contents, fitting together in capsule fashion. The charged capsules in many cases were enclosed in a somewhat larger container, with more of the powdered charge packed around the capsule, to isolate further the inner charge and cut down the possibility of composition change by diffusion through the water vapor (see Bowen and Tuttle, 1950). The charge was then placed either in a Morey-type bomb with a measured quantity of water or in a small bomb of the Tuttle-type apparatus. In the sealed 18-ml. bombs the pressure is a function of the quantity of water in the bomb and of the temperature and can be determined readily by reference to the curves and tables prepared by Kennedy (1950). At subcritical temperatures standard steam tables are useful. In the Tuttle ap-

[3] Spectrographic analysis by Oiva Joensuu.

paratus water is pumped directly into the bomb with a high-pressure pump, and the pressure is read on a Bourdon gauge mounted in the line.

Upon completion of a run, the Morey-type bombs were quickly cooled to room temperature with a water quench and the small bombs with a forced-air quench, although it is very doubtful that rapid cooling is at all essential in the present investigation. The charges were examined optically, and an X-ray powder picture of each was made. Optical examination has been of very limited value in this system, as the products are generally so fine-grained that positive identification cannot be made with the microscope. It is doubtful that any reliable identification could have been made without the use of X-ray diffraction.

THE HEXAGONAL POLYMORPH OF ANORTHITE

Only one modification of the composition $CaAl_2Si_2O_8$, the triclinic mineral anorthite, has been known either in nature or as a synthetic product. Several years ago, when this investigation was begun, oxide mixtures and glasses of the anorthite composition, crystallized hydrothermally at low temperatures, were found to produce a crystalline substance with an X-ray diffraction pattern that did not correspond to any known substance in the system CaO-Al_2O_3-SiO_2-H_2O. The product of these low-temperature runs was so fine-grained that microscopic observation was useless; whether the material was a single crystalline phase or a mixture of crystalline phases or whether some uncrystallized glass remained in the cases where glass was used was doubtful even at high magnifications. A "bulk" index of refraction of approximately 1.565 was determined, but no significance could be attached to this value; individual grains could not be detected. The isotropic-appearing clump of material observed under the microscope showed lowest relief in an oil of this refractive index. The X-ray diffraction lines were sharp, however, indicating that a well-crystallized phase was present. Some runs produced anorthite, some a mixture of anorthite and the unknown material, and others just the unknown material; yet all of these looked much the same under the microscope.

The unknown material did not lose weight when strongly heated; it was, therefore, anhydrous. The X-ray powder pattern could not be accounted for by any known mixture of phases in the system CaO-Al_2O_3-SiO_2, and the relatively simple diffraction pattern suggested that a single phase was present—a hitherto unknown modification of $CaAl_2Si_2O_8$. The unlikely possibility remained, however, that two or more unknown and unresolved crystalline substances were present in the runs.

The situation was clarified when word was received from the Geophysical Laboratory of Washington[4] that G. L. Davis had analyzed two unidentified compounds and found them to be of the same composition as anorthite. These two compounds were accidentally produced by L. B. Wyckoff (now retired), of Union Carbide and Carbon. The X-ray powder pattern of one of these compounds proved virtually identical with that of the unknown material; the very fine-grained product was thus unquestionably shown to be a single crystalline phase. Full details of Wyckoff's synthesis and of the properties of the two compounds will be given in a separate publication by Davis and Tuttle. Co-crystallization of the two compounds took place meta-

[4] Written and oral communications with G. L. Davis, O. F. Tuttle, and N. L. Bowen.

stably when a graphite crucible melt of approximately the composition of anorthite was cooled to and held at 1,250° C., between measurements that were being made on the viscosity of the melt. The two phases were observed to be more or less segregated in the crucible as clusters of megascopic crystals. Davis and Tuttle found both compounds to have the same composition, $CaAl_2Si_2O_8$, and therefore to be polymorphs of anorthite. One of the polymorphs is hexagonal,[5] the other orthorhombic.

The hexagonal modification proved to be the same as the product obtained in certain hydrothermal syntheses to be described here. The refractive indices (as determined by Davis and Tuttle on Wyckoff's large crystals) are $\omega = 1.585$ and $\epsilon = 1.590$. The values for anorthite are $\alpha = 1.576$, $\beta = 1.584$, and $\gamma = 1.588$. The similarity of refractive indices would indicate that the densities of anorthite and hexagonal $CaAl_2Si_2O_8$ are much the same.

THE EXPERIMENTAL DATA

RUNS WITH GLASS AND OXIDES (TABLE 1)

When experimental work was begun, short runs of 24 hours or less were made, generally at approximately 1,000 bars pressure. In all runs at temperatures above approximately 375° C. (using glass or oxide mixtures of the anorthite composition), anorthite was formed.[6] In the temperature range 300°–375° C., hexagonal $CaAl_2Si_2O_8$ was formed, commonly accompanied by varying (and unpredictable) amounts of anorthite. The presence of the two polymorphs over a range of temperature is indicative of nonequilibrium conditions. In addition, a few duplicate runs indicated that considerably different proportions of anorthite and hexagonal $CaAl_2Si_2O_8$ could be produced in short runs under the same P-T conditions. Thus anorthite, but not hexagonal $CaAl_2Si_2O_8$, was observed to form above 375° C., and the hexagonal modification with or without some anorthite formed below this temperature. Apparently, below 375° C. hexagonal $CaAl_2Si_2O_8$ has a greater initial tendency to crystallize than does anorthite, although the varying anorthite percentage can indicate

TABLE 1*

RUNS WITH GLASS AND OXIDES OF ANORTHITE COMPOSITION

Temp. (° C.)	Time (Hours)	H_2O Pressure (Bars)†	Products‡	Original Material
504...	24	1,000	An	Oxides
465...	121	425	An	Glass
410...	24	1,000	An	Glass
408...	168	310	An	Glass
408...	168	310	An	Oxides
380...	24	1,000	An	Glass
370...	280	220	An	Oxides+LiCl flux
368...	24	1,000	An+Hex.	Glass
362...	48	190	Hex.+An	Oxides+LiCl flux
360...	156	190	Hex.+An	Oxides
358...	193	185	Hex. (trace An?)	Glass
355...	24	1,000	Hex.+An	Glass
352...	193	165	Hex.	Glass
350...	27	1,000	Hex. (trace An?)	Glass
350...	50	1,000	An+some Hex.	Glass
332...	750	130	Hex.+An.	Oxides
305...	6	1,000	Hex.+An.	Glass
300...	24	1,000	An+Hex.	Glass
300...	5	1,000	Hex.	Glass
303...	204	90	Hex.	Glass
235...	48	32	Hex.	Glass
220...	60	24	Hex.	Glass

* Summary of more significant experimental runs.

† Runs at 1,000 bars were made in Tuttle-type apparatus; all others in Morey-type bombs.

‡ An = anorthite, Hex. = hexagonal $CaAl_2Si_2O_8$.

[5] The structure of hexagonal $CaAl_2Si_2O_8$ will be separately described by G. H. Donnay. In a very recent short note (Donnay, 1952) the most probable space group was published; it is stated to be not isostructural with hexagonal $BaAl_2Si_2O_8$, or "α-celsian," as originally it was thought to be (see Ito, 1950).

[6] In the lower-temperature ranges the oxide mixtures, however, were for the most part incompletely reacted.

that initial nucleation probably influences the crystallization process; under conditions of rapid crystallization it is likely that, once nucleation takes place, that phase that begins to crystallize has a tendency to continue to do so, even though it may be metastable.

Because low-temperature reactions were very slow, longer runs were made. In runs up to 2 weeks (and longer in several cases) very much the same results were obtained: anorthite alone appeared at temperatures above approximately 375° C.; below this temperature, hexagonal $CaAl_2Si_2O_8$ with or without anorthite was produced. At lower temperatures, of approximately 300° C., hexagonal $CaAl_2Si_2O_8$ is formed either alone or with very small amounts of anorthite, except in short runs, in which the anorthite content may be appreciable. Whether anorthite, once formed, is transformed to hexagonal $CaAl_2Si_2O_8$ in the longer runs near 300° C. or whether, by coincidence, less anorthite nucleation took place in these particular experiments is still uncertain.

RUNS WITH HEXAGONAL $CaAl_2Si_2O_8$

A group of experiments was performed with hexagonal $CaAl_2Si_2O_8$ as the initial experimental material, to determine under what conditions it can be transformed to another phase or phases. In this way uncertainties due to initial metastable nucleation may be avoided. Fine-grained material produced hydrothermally for the purpose was used, as well as samples crushed from the large, micaceous crystals synthesized by Wyckoff.[7]

The data on these runs are summarized in table 2. It is apparent that the hexagonal modification is converted to anorthite at temperatures of 400° C. and higher. The change, when it takes place in the larger crystals produced by Wyckoff, can be observed under the microscope as a recrystallization; the original material is reduced to a fine-grained aggregate of anorthite. No change was observed in hexagonal $CaAl_2Si_2O_8$ when held below approximately 400° C., possibly because of insufficient time at the lower temperature.

It is perhaps worth noting that in the runs made in the Tuttle-type apparatus (1,000 bars pressure) the transformation to anorthite appears to be slowed or inhibited.

TABLE 2

RUNS WITH HEXAGONAL $CaAl_2Si_2O_8$

Temp. (° C.)	Time (Hours)	H_2O Pressure (Bars)	Products	Original Material
461	168	420	An	Wyckoff's crystals
453	168	1,000	An+Hex.	Fine-grained crystals*
425	240	1,000	Hex. (unchanged)	Wyckoff's crystals
400–406	168	305	An	Wyckoff's crystals
400	168	1,000	Hex. (+trace An?)	Fine-grained crystals*
340–355	432	180	Hex. (unchanged)	Wyckoff's crystals
327–332	1,152	130	Hex. (unchanged)	Wyckoff's crystals
316–325	336	120	Hex. (unchanged)	Wyckoff's crystals+ trace $FeCl_3$

* Prepared by hydrothermal synthesis.

[7] Kindly supplied by Davis and Tuttle, along with crystals of the orthorhombic modification of $CaAl_2Si_2O_8$.

RUNS WITH ORTHORHOMBIC $CaAl_2Si_2O_8$

Some experiments were also carried out with the orthorhombic modification of $CaAl_2Si_2O_8$, to evaluate better the stability relations of anorthite and the hexagonal polymorph. As pointed out above, the use, as starting materials, of phases other than those involved in the reactions studied is often advantageous. (It was here assumed that orthorhombic $CaAl_2Si_2O_8$ is unstable under the conditions of this investigation; it was found to be unstable at higher temperatures by Davis and Tuttle (personal communication).

Table 3 lists the runs in which the orthorhombic polymorph (produced by Wyckoff) was used as the starting material. Above approximately 350° C., orthorhombic $CaAl_2Si_2O_8$ is converted to anorthite. It is noteworthy that the 175-hour run, at 400°–406° C., produced hexagonal $CaAl_2Si_2O_8$. In table 2 is listed a run of the hexagonal material, made under the same conditions (the two bombs were run in the same furnace and for the same time), which produced anorthite. Evidently, the orthorhombic plymorph was transformed to the hexagonal polymorph, whereas the hexagonal polymorph changed to anorthite. The following run, in table 3 (400° C., for 353 hours), shows that, given more time, conversion to anorthite does take place. It is not known whether or not the formation of hexagonal $CaAl_2Si_2O_8$ always takes place at these low temperatures as an intermediate step in the change of the orthorhombic modification to anorthite. At approximately 330° C. or below, orthorhombic $CaAl_2Si_2O_8$ remains unchanged for 1½ months, although the last run in table 3 indicates that a flux ($FeCl_3$, in addition to water) produces conversion to anorthite at 325° C. A run made under identical conditions, using hexagonal $CaAl_2Si_2O_8$ plus $FeCl_3$, remained unchanged, however (see table 2). No runs below this temperature were made with the orthorhombic material.

TABLE 3

RUNS WITH ORTHORHOMBIC $CaAl_2Si_2O_8$

Temp. (° C.)	Time (Hours)	H_2O Pressure (Bars)	Products	Original Material
450	168	410	An	Orthorhombic crystals
400–406	175	305	Hex.	Orthorhombic crystals
400	353	290	An	Orthorhombic crystals
340–355	432	180	An	Orthorhombic crystals
340–345	175	160	Orthorhombic crystals (unchanged)	Orthorhombic crystals
327–332	1,152	130	Orthorhombic crystals (unchanged)	Orthorhombic crystals
316–325	336	120	An+some unknown material	Orthorhombic crystals+$FeCl_3$

THE PROBLEM OF THE STABILITY OF HEXAGONAL $CaAl_2Si_2O_8$

The stability relations of minerals such as zoisite and lawsonite are not known except in a qualitative way as deduced from field evidence. No valid synthesis of either of these two minerals is known to the authors, and they were not produced in this investigation. This fact does not preclude the possibility that one or the other might have a field of stability that includes some of the pressure-temperature-composition range here studied; this point will be considered at another time.[8]

[8] See n. 2, p. 387.

The problem to be considered is whether either anorthite or hexagonal $CaAl_2Si_2O_8$ is stable under the conditions in which they have been produced in this investigation.

In considering the relations between the hexagonal and anorthite forms of $CaAl_2Si_2O_8$, the effect of pressure is not important from an equilibrium viewpoint. Both forms are anhydrous, and the densities of the two are approximately the same. The role of water is principally that of a flux, and no systematic effect of water pressure on the formation of either compound was observed, although it may have an effect on reaction speeds.

TABLE 4

INITIAL MIXTURE OF CO-CRYSTALLIZED ANORTHITE AND HEXAGONAL $CaAl_2Si_2O_8$

Temp. (° C.)	Time (Months)	H_2O Pressure (Bars)	Results
350	3	170	Anorthite
300	3	87	Anorthite+Hex. (see text)

CONSIDERATION OF THE EXPERIMENTAL DATA

On the basis of the runs made with glass, oxides, and the hexagonal polymorph itself, one might infer that hexagonal $CaAl_2Si_2O_8$ is stable below approximately 375° C. and that anorthite, when produced below this temperature, persists metastably. Hexagonal $CaAl_2Si_2O_8$ was not observed to crystallize under hydrothermal conditions at temperatures above approximately 375° C., and it is definitely converted to anorthite at and above 400° C. At temperatures below 375° C. the hexagonal material was invariably produced, with or without anorthite. These data, however, are insufficient to establish the stability relations in the system below 375° C. One cannot, for example, state with certainty that in any of the above experiments anorthite was converted to the hexagonal phase. A phase transition that can be reversed is considered one of the best criteria for equilibrium. In all but the rapid alpha-beta type inversions, however, it is generally much more difficult to induce the change in the down-temperature direction (i.e., to produce the lower-temperature from the higher-temperature form). In general, it is much easier to increase the entropy of any system than to decrease it, and many cases are known in which a stable low-temperature phase or phase assemblage cannot be experimentally produced from the high-temperature phase or phase assemblage. If one assumes that hexagonal $CaAl_2Si_2O_8$ is a stable low-temperature modification of anorthite, it would therefore not be at all surprising to find anorthite persisting metastably in the temperature range in which the hexagonal polymorph should be produced, particularly in view of the low solubility of $CaAl_2Si_2O_8$ and of the low temperatures involved.

Because of the uncertainties apparent in the above data, several longer runs were made. The starting material consisted of a submicroscopically fine intergrowth of anorthite and the hexagonal modification, co-crystallized from a glass. If both phases were initially present (in known concentrations), the more stable of the two might tend to form at the expense of the less stable more readily than either phase alone might transform. Thus, in addition to both phases being present as "seed," the intimate mixture of finely crystalline nature should also favor any change. In table 4 are listed two runs of 3 months each.

At 350° C. the mixture was completely converted to anorthite. The interpreta-

tion of the run at 300° C. is somewhat uncertain, as an X-ray photograph of the uppermost portion of the charge in the small crucible showed almost complete conversion to anorthite, whereas the lower part of the charge showed some increase in the proportion of the hexagonal polymorph. The effect of fluid transfer and reprecipitation is unknown.

Apparently, the hexagonal $CaAl_2Si_2O_8$ is unstable with respect to anorthite at 350° C., and in shorter runs it is crystallized as a metastable compound at this and slightly higher temperatures. The meaning of the data below 350° C. is still uncertain; the run at 300° C. might be interpreted as signifying that this temperature represents approximately that of an inversion from the hexagonal to the triclinic forms. However, the very sluggish nature of the inversion (involving structural breakdown and recrystallization), particularly at low temperatures, makes this interpretation uncertain; considerably longer times might be necessary to establish equilibrium.

ADDITIONAL CONSIDERATIONS ON HEXAGONAL $CaAl_2Si_2O_8$

The experimental data show hexagonal $CaAl_2Si_2O_8$ to be unstable above 350° C. The data on hand do not justify definite conclusions as to its stability at lower temperatures, particularly at or below 300° C. To evaluate the relations in the system $CaAl_2Si_2O_8$-H_2O, it is, of course, essential to know whether or not this modification has any field of stability at all.

The hexagonal modification of $CaAl_2Si_2O_8$ is unknown as a mineral—if it exists in nature, it has not been reported. Its absence or rarity in nature is perhaps a very good argument against its having a stable field of existence. It is possible, however, that, even though stable, it might not readily form under natural conditions. It is anhydrous, whereas the "breakdown" products (or low-temperature "equivalents") of anorthite in nature contain water. The role of water in the hydrothermal synthesis of hexagonal $CaAl_2Si_2O_8$ is probably merely that of a flux. Thus it is not inconceivable that hexagonal $CaAl_2Si_2O_8$ represents the low-temperature modification of anorthite stable in the *absence* of water; the hydrated phases found in rocks are stable in the chemical environment, containing H_2O as well as other components that exist in nature. It is doubtful that at and below 300° C. any reactions in silicates take place in the absence of fluxes—on this basis it might be argued that hexagonal $CaAl_2Si_2O_8$ would not be crystallized in a metamorphic process. At temperatures sufficiently low, in the absence of water, reaction would not take place; at higher temperatures anorthite would be formed. In like fashion anorthite, held in the dry state at these low temperatures, would also not be expected to change. If water is present, as it probably always is at these temperatures, a hydrate might logically be produced. The additional components present in nature may also eliminate or pinch out the stability field of the hexagonal modification, assuming that one exists. This explanation does not, however, account for the failure to produce forms such as zoisite and lawsonite in the experimental investigation.

Hexagonal $CaAl_2Si_2O_8$ might also have a low-temperature limit of stability. If it thus has a small stable range, delimited by anorthite at higher temperatures and by another phase or phases at lower temperatures, it would be expected to be rare in nature.

Possibly hexagonal $CaAl_2Si_2O_8$ is metastable at all temperatures, but more stable than anorthite below 300° C. This

is another way of saying that below 300° C. the hexagonal polymorph has a lower free energy than anorthite but that there is another form or assemblage of forms that has a still lower free energy, yet for some reason is not realized experimentally.

In compounds exhibiting polymorphism, the low-temperature modifications generally have lower symmetry

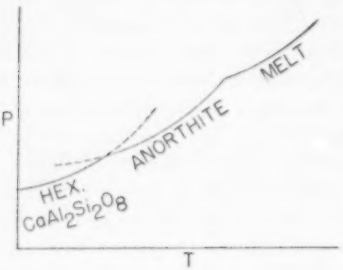

FIG. 1.—Imaginary vapor-pressure curves of $CaAl_2Si_2O_8$, assuming the hexagonal modification to be stable.

than the high-temperature forms. Anorthite is stable at high temperatures, whereas hexagonal $CaAl_2Si_2O_8$ (of higher symmetry), if it is stable at all, must be a low-temperature modification. The density relations must be considered, however, and the hexagonal modification has higher refractive indices than does anorthite. In lieu of an accurate density measurement, the refractive indices can be taken as evidence that anorthite has a lower density than the hexagonal polymorph. The relative densities are thus an indication that the hexagonal form is stable at low temperatures.

If hexagonal $CaAl_2Si_2O_8$ is a low-temperature modification of anorthite, the diagrammatic vapor-pressure curves would be as in figure 1. The dotted curves represent metastable extensions of hexagonal and triclinic $CaAl_2Si_2O_8$ above and below their respective stable-temperature ranges. Figure 2 represents the hexagonal form as a metastable compound at all temperatures. Hexagonal $CaAl_2Si_2O_8$ is definitely observed to crystallize metastably, i.e., above the inversion point (~300° C.?) of figure 1. The low-temperature stability of this form might be questioned on the basis that silicates are rarely produced above their stable-temperature range. The other alternative, that hexagonal $CaAl_2Si_2O_8$ is unstable under all conditions, does not satisfy this criticism, however, as the formation of a compound *above* its stability field is no less likely than the formation of a compound with *no* range of stability (as in fig. 2). The low temperatures and extreme sluggishness in terms of atomic or ionic movement might well explain the tendency to form hexagonal $CaAl_2Si_2O_8$ metastably, or above its stability field. This effect

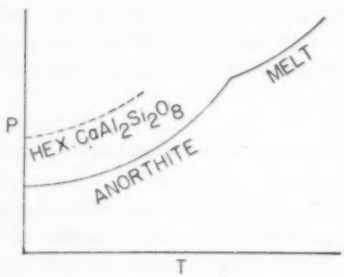

FIG. 2.—Imaginary vapor-pressure curves of $CaAl_2Si_2O_8$, assuming the hexagonal modification to be metastable at all temperatures.

would be enhanced if the free energies of anorthite and the hexagonal form were not greatly different in the temperature range considered.

The question of whether or not hexagonal $CaAl_2Si_2O_8$ accepts Na and Si in solid solution in place of Ca and Al will not be discussed here. The hexagonal modification can be produced along with plagioclase from anorthite-rich plagio-

clase glasses, but a discussion of the still somewhat uncertain data will be deferred until additional work is done on the whole plagioclase series.

CONVERSION OF LAWSONITE TO HEXAGONAL $CaAl_2Si_2O_8$

Hexagonal $CaAl_2Si_2O_8$ is produced when the mineral lawsonite is thermally decomposed. Crushed lawsonite,[9] heated in air for 24 hours at 650° C., is completely transformed to submicroscopic hexagonal $CaAl_2Si_2O_8$. Above approximately 800° C., anorthite begins to form in 24-hour heating periods, and at 1,050° C., the conversion to anorthite is complete in 4 hours or less.

The hexagonal modification is produced at these temperatures as a metastable phase concurrently with the lawsonite breakdown, as X-ray photographs of samples heated for 24 hours in the range 550°–600° C. show mixtures of as yet unaltered lawsonite plus hexagonal $CaAl_2Si_2O_8$. In 24 hours at 500° C., using a trace of LiF as a flux, some hexagonal $CaAl_2Si_2O_8$ was produced, as was also a faint trace of anorthite. The lowest temperature at which lawsonite decomposes in air in a reasonable time has not yet been established, and no hydrothermal work has yet been done. Additional experimentation on this recently observed breakdown behavior of lawsonite will be later reported.

THE LOW-TEMPERATURE STABILITY OF ANORTHITE

The anorthite-H_2O relations at high temperatures have not been investigated, but the data on hand indicate anorthite to be stable up to its melting point in the presence of water. In this investigation, only solid phases (neglecting the vapor) are involved, because the refractory nature of anorthite makes hydrothermal experimentation out of the question with the present equipment at temperatures involving the melt.

The data relevant to anorthite are contained in tables 1–4. Anorthite is observed to crystallize in the presence of H_2O at temperatures down to 300° C. Above 375° C. it is the only crystalline phase obtained. The runs in table 4 show that hexagonal $CaAl_2Si_2O_8$ is converted to anorthite at 350° C.; at 300° C. the results are somewhat uncertain, although in a portion of the sample anorthite was observed to be formed at the expense of the hexagonal modification. In table 3 it is seen that the orthorhombic modification of $CaAl_2Si_2O_8$ is converted to anorthite at 355° C. and, in the presence of a small amount of $FeCl_3$ in addition to water, is changed to anorthite at 325° C.

A few runs had been made earlier with powdered natural anorthite and are listed in table 5. The 3-month run at 347°–357° C. utilized very finely crystalline synthetic anorthite, prepared initially by hydrothermal crystallization of glass. In none of these runs could any change be detected in the anorthite. As pointed out earlier, however, the failure of anorthite to change is not in itself proof of its stability.

The tendency for high-temperature modifications to be produced and to persist below their field of stability is quite pronounced in silicates that undergo reconstructive polymorphic transformations. The fact that anorthite is produced in long runs at 350° C. from a variety of original materials is, however, rather convincing evidence of its stability at this temperature. The conversion of the orthorhombic modification to anorthite below 350° C., as well as the 3-month run of

[9] Kindly supplied from the type locality by Professor A. Pabst.

the anorthite-hexagonal phase mixture might indicate that the range of stability may extend to a temperature as low as 300° C. It should again be pointed out that the stability of anorthite is considered only within the simple system $CaAl_2Si_2O_8$-H_2O. Either deviation from the CaO-Al_2O_3-SiO_2 ratios here considered or the introduction of additional chemical components introduces the possibility of new phase formation, with the subsequent probability that the stability range of anorthite will be impinged upon.

Confirmatory evidence for the relatively low-temperature hydrothermal stability of anorthite can be found in the experiments of F. H. Norton (1937). Natural anorthite (also from Miakejima, Japan) was finely pulverized and placed in a reaction chamber with H_2O and CO_2; the apparatus was constructed to reflux the solution over the anorthite so as to prevent "stagnation." Norton's tabulated data for anorthite are reproduced in table 6. The breakdown products were identified by Norton as calcite and pyrophyllite (?). These data can be interpreted as indicating that anorthite is stable above 300° C. in a hydrous environment, even in the presence of CO_2. The run at 275° C. shows "considerable alteration"; yet at 300° C. no change is observed in the anorthite. The 250° C. run would indicate that at so low a temperature more time is necessary to produce the amount of alteration observed at 275° C.

TABLE 5

RUNS WITH CRYSTALLINE ANORTHITE

Temp. (° C.)	Time	H_2O Pressure (Bars)	Products	Original Material
347–357	3 months	180	An (unchanged)	Synthetic An
353	168 hours	170	An (unchanged)	Miakejima An
355	240 hours	170	An (unchanged)	Miakejima An
346	381 hours	150	An (unchanged)	Miakejima An
303	168 hours	90	An (unchanged)	Miakejima An

TABLE 6

Temp. (° C.)	CO_2 Pressure (Cold)	Total Pressure (Lb/In²)	Time (Days)	Conversion
300	260	1,950	18	No change
250	300	1,230	23	Slight change
275	300	1,650	24	Considerable change

ZEOLITE FORMATION

Very few data have been obtained at temperatures below 300° C. Several runs of short duration have produced what appears to be thomsonite at temperatures slightly above 200° C. Several other runs produced only hexagonal $CaAl_2Si_2O_8$, and in one experiment a mixture of the two was obtained. Any conclusions as to zeolite stability in this system must await further experimentation.

SUMMARY AND CONCLUSIONS

The experimental evidence indicates that pure anorthite is stable at temperatures down to 350° C., and possibly as low as 300° C. in the presence of H_2O. The H_2O pressures ranged from that of the vapor pressure of water at the experimental temperatures up to 1,000 bars. A hexagonal polymorph of anorthite is con-

sistently produced from glasses and oxide mixtures in the system $CaAl_2Si_2O_8$-H_2O below approximately 375° C. In the temperature range 300°–375° C. it is generally co-crystallized with anorthite, but it appears to be unstable with respect to anorthite, at least in the upper portions of the temperature range. Hexagonal $CaAl_2Si_2O_8$ may be stable (particularly in an anhydrous system) below 300° C.; the present evidence is not conclusive, although this modification is unknown in nature. The high-density hydrous phases zoisite and lawsonite were not encountered in this investigation.

Additional experimental work is necessary to evaluate with certainty the equilibrium relations. Unfortunately, the experiments must be of very long duration, as the low temperatures and low solubilities inherent in this study made for exceedingly slow reaction and a tendency for persistence of metastable phases. Very long runs (principally at temperatures below 300° C.) will be made on anorthite and mixtures of anorthite and hexagonal $CaAl_2Si_2O_8$. In addition, thermochemical data on hexagonal $CaAl_2Si_2O_8$ (and also on lawsonite and zoisite) would be helpful.

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GEOLOGICAL NOTES

CLASSIFICATION OF THE WISCONSIN GLACIAL STAGE[1]

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Leighton (1933) presented a fourfold classification of the Wisconsin glacial stage that generally has been accepted by Pleistocene geologists (see fig. 1). Apparently no significant stratigraphic break was recognized within the stage.[2] One may infer from an earlier publication by Leighton (1931, pp. 51–53) that classification was based upon organization of centers of ice accumulation and that significant breaks within the sequence were the result of such organization and reorganization. For example, the Iowan drift deposited in Minnesota and Iowa was the result of Manitoban [Keewatin] glaciation; the Tazewell and Cary drifts (early and middle Wisconsin) of the western Great Lakes Basin were the result of Quebecan [Labradorian] advance; and the Mankato (late Wisconsin) drift of the Missouri-Mississippi–Great Lakes basins was the result of Hudsonian [Laurentide] advance. Antevs (1945, pp. 2–8) supported this hypothesis.

In Minnesota, with the exception of the east-central and northeastern parts, and in Iowa, only two advances of Wisconsin glacier ice were recognized, namely, the Iowan and the Mankato. Kay and Leighton (1933, pp. 673–674) proposed that the positions of the Tazewell and Cary were occupied by the Peorian loess in Iowa. Kay and Graham (1943, p. 156) introduced the term "Peorian intraglacial subage" for the time of deposition of the Peorian loess and weathering of the loess prior to the deposition of the Mankato drift (see fig. 1). A leached zone that occurs in the upper part of the Peorian loess and that is overlain by "Mankato" till probably would represent weathering during Tazewell or Cary time. The present writer (Ruhe, 1950*b*) believes that the Mankato till of the sections reported by Kay and Graham (1943, pp. 211–217) is Cary.

Schultz and Stout (1945, pp. 241, 243) recognized a stratigraphic break in the loess overlying the Loveland loess in Nebraska. A Bignell loess and a Peorian loess separated by a soil profile were recognized. Schultz and Stout proposed the correlation given in figure 1. The Bignell loess was believed correlative of the Mankato; the buried soil (soil *X*) was correlated with the Two Creeks forest bed (Cary-Mankato interval); and the Peorian loess was believed to be the equivalent of the Peorian loess of Iowa. Schultz and Stout (1948, p. 570) later named the buried soil separating the Bignell and Peorian loesses the "Brady soil." Condra, Reed, and Gordon (1947, pp. 45–46) concurred in correlation of loessial horizons in Nebraska.

Frye and Fent (1947, pp. 45–51) and Frye and Leonard (1949, pp. 890–898) recognized a twofold division of the loess above the Sangamon soil profile on Loveland loess in Kansas and correlated the lower member with the Peorian loess of Nebraska and the upper member with the Bignell loess of Nebraska. Frye and others (1949, p. 56) restricted the Peoria silt [loess] to the Iowan and Tazewell, but considered the Bignell correlative of the Mankato (see fig. 1).

[1] Manuscript received May 28, 1951.

[2] Leighton (1931, pp. 45–51) recognized a faint profile of weathering at the top of the Peorian (Iowan) loess, where it is overlain by early Wisconsin (Tazewell) till, and concluded that the Iowan and early Wisconsin were closely related in time.

Ruhe (1950*a*) recognized four Wisconsin drifts—Iowan, Tazewell, Cary, and Mankato—in northwestern Iowa and demonstrated a major twofold division of the Wisconsin drifts on a basis of a statistical analysis of the drift topographies. The major time break was shown to be the Tazewell-Cary interval. No evidence was found to show comparable time breaks that represented the Iowan-Tazewell or Cary-Mankato intervals.

Flint (1950) recognized a major twofold division of the four drifts of the Wisconsin in South Dakota and concluded that the Iowan and Tazewell were closely related in time and that the Cary and Mankato were a second closely related pair.

Ruhe (1950*b*) correlated a buried soil that stratigraphically separates the Wisconsin loess in western Iowa into two components with the Tazewell-Cary interval and suggested that the Brady soil of Nebraska and Kansas was correlative (see fig. 1).

Leonard (1950) presented faunal studies to show the subdivision of the Peorian loess of Kansas into three zones. The lowest zone, barren of fauna, was tentatively correlated with the Farmdale of Illinois (Leighton and Willman, 1950, pp. 602–603). The lower faunal zone was correlated with the Iowan, and the upper faunal zone with the Tazewell. Leonard suggested that the Bignell loess may represent the time of both Cary and Mankato.

Frye (in Moore and others, 1951, p. 14) assigned the Peoria loess of Kansas to the Iowan and Tazewell, and the Bignell loess to the Cary and Mankato.

Ruhe (1951) pointed out that the Cary drift surface in northwestern Iowa and southwestern Minnesota is differentiated from the Tazewell and other adjacent older drift surfaces by a marked erosional topographic discontinuity.

Flint (1950) and Ruhe (1950*b*) correlated the Wisconsin drifts of eastern South Dakota, southwestern Minnesota, and northwestern Iowa. The present writer has completed regional mapping of the Wisconsin

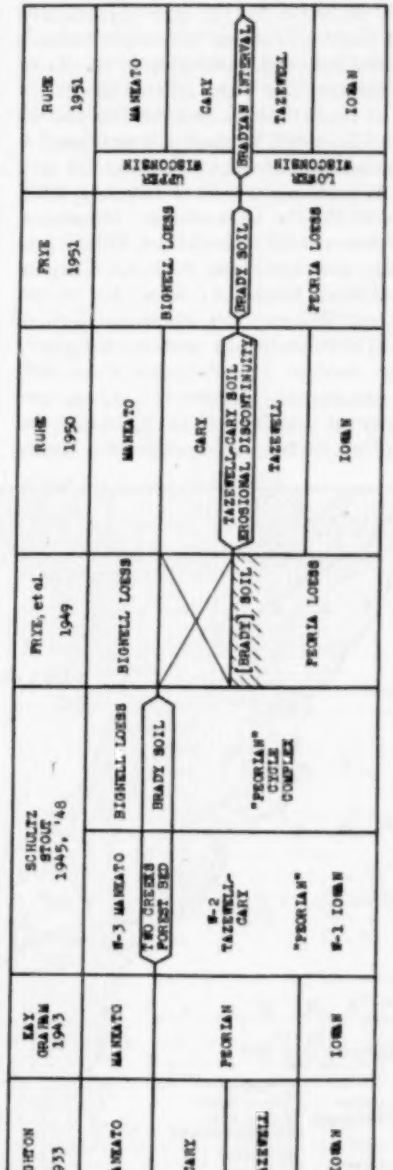

Fig. 1.—Comparison of classifications of the Wisconsin glacial stage.

drifts in north-central and northeastern Iowa and southeastern Minnesota under a National Research Fellowship in the Natural Sciences. The Cary drift of the James lobe of South Dakota and the Des Moines lobe of Iowa and Minnesota is stratigraphically overlapped by the Patrician Cary drift (the Wisconsin red drift of Leverett, 1932, pp. 39–56) in east-central Minnesota. Thwaites (1945) and Ekblaw (1945) previously correlated the Patrician Cary of east-central Minnesota with the "type" Cary of Illinois. The Mankato drift of Flint (1950) and Ruhe (1950*b*) stratigraphically overlaps the Patrician Cary drift of east-central Minnesota. Contemporaneity of activity of the Keewatin and Patrician centers of ice dispersion during Cary and Mankato time is shown by the stratigraphic overlap of the Keewatin Cary drift of the Des Moines lobe by the Patrician Cary, the St. Croix moraine, and the overlap of the Patrician Cary by the Keewatin Mankato, the Altamont moraine of the Des Moines lobe. No soil or weathering profiles were found between any two of these drifts.[3] (Compare these relationships with the concepts of Leighton, 1931.) Thus regional correlations of the Wisconsin drifts of the Mis-

[3] These Cary and Mankato relationships were demonstrated in a field conference of the Midwest Section of the Friends of the Pleistocene in Dakota County, Minnesota, during May 11–13, 1951. Approximately forty Pleistocene geologists and soil scientists from Illinois, Iowa, Michigan, Minnesota, Nebraska, and Wisconsin reviewed this evidence in the field.

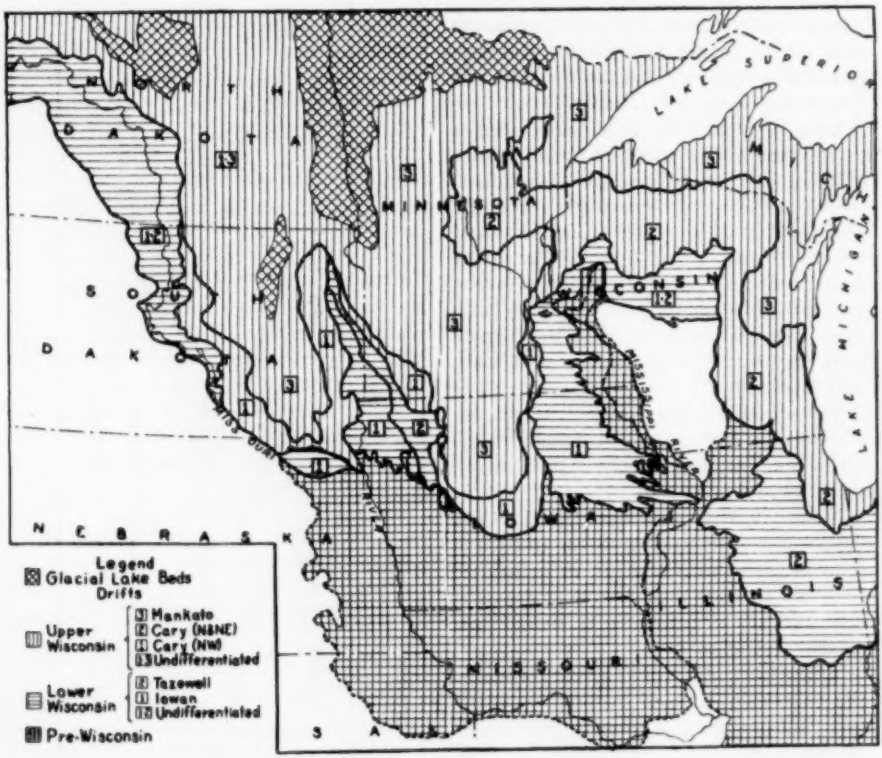

FIG. 2.—Correlation and regional distributions of the Wisconsin drifts of the Missouri-Mississippi–western Great Lakes basins. (South Dakota after Flint, 1950; northwestern and north-central Iowa and southern Minnesota, Ruhe; other areas after Glacial Map of North America.)

souri-Mississippi–western Great Lakes basins are established.

All these recent studies by the geologists cited show that the Wisconsin glacial stage is a major twofold division of drifts or loess equivalents. Within each division is an association of drifts and/or loesses that are closely related in time. The major break in the sequence is the Tazewell-Cary interval and was long enough in time to allow alteration of the Tazewell loess by weathering processes (Brady soil genesis) prior to deposition of Cary loess, and to allow marked erosional modification of the Tazewell drift surface by subaerial processes prior to the deposition of Cary till. Current opinion places the Brady soil as a correlative of the Tazewell-Cary interval rather than the Two Creeks forest bed (Cary-Mankato interval), as originally defined by Schultz and Stout. It is suggested here that the name "Bradyan interval" be applied to the major break in the Wisconsin sequence, the Tazewell-Cary interval. The Bradyan interval separates the Wisconsin glacial stage into Lower Wisconsin, including the Iowan and Tazewell, and Upper Wisconsin, including the Cary and Mankato (see fig. 1).

The Farmdale loess of Illinois (Leighton and Willman, 1950, pp. 602–603) has not been included in figure 1. Because the weathering profile on the Farmdale loess and beneath the Iowan loess is very youthful and records only a brief interval when compared to the Sangamon profile on the Illinoian drift, Leighton and Willman (1950, p. 603) concluded that the Farmdale loess is pro-Wisconsin in age.

Correlation and regional distributions of the Lower and Upper Wisconsin drifts of the Missouri-Mississippi-western Great Lakes basins are shown in figure 2.

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DISCUSSION

THE MECHANICAL ANALYSIS OF SEDIMENTS FROM THIN-SECTION DATA: A DISCUSSION[1]

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Greenman's method (1951) for calculating the true frequencies of particle sizes from measurements made in thin section is a valuable extension of Krumbein's theory. Unfortunately, Greenman does not discuss the random or systematic errors which may affect the results obtained by his procedures. Because some of these, depending on the type of information the investigator is seeking, are substantial in terms of the errors associated with counts of whole particles, a detailed consideration of this aspect of the problem may prove helpful to those who must resort to size measurements in thin or polished sections. A portion of this discussion is necessarily somewhat technical, but the reader who is disinclined to follow the mathematical argument may turn to the last paragraphs, where the practical implications of the theory are summarized.

Considering only logarithmic grade scales, we note that Greenman's expression for the distribution function of sectioned grain diameters in terms of whole-grain size frequencies and certain constants may be written in at least two other ways. The first of these relates the frequency of the ith thin-section class to the frequencies of one or more whole-grain size classes:

$$\begin{aligned} Q_0 &= T_0 F(r_0), \\ Q_1 &= T_0 F(r_1) + T_1 F(r_0), \\ &\vdots \\ Q_i &= \sum_{k=0}^{i} T_k F(r_{i-k}). \end{aligned} \tag{1}$$

Here, as elsewhere in this discussion, Greenman's notation has been changed in order to simplify the symbolic statements: index zero identifies the largest size occurring in the respective populations, whether whole-grain or thin-section; index 1, the next smaller size, and so on.

[1] Manuscript received December 26, 1951.

The Q_i are sectioned-grain size frequencies, the $F(r_{i-k})$ are whole-grain size frequencies, and the T_k are constants which can be calculated from the M's of Greenman's equations by the formula:

$$T_k = M_{k+1} - M_k .$$

Values of the T_k and all other constants mentioned below are listed in table 1 for the case of

TABLE 1

VALUES OF THE CONSTANTS
($\phi/2$ Class Interval)

INDEX (k)	CONSTANT				
	T_k	W_k	V_k	U_k	R_k
0	0.7071	+1.4142	1.414	−0.4142	0.414
1	0.1589	−0.3178	0.389	−0.0964	0.168
2	0.0694	−0.0673	0.158	−0.0291	0.078
3	0.0328	−0.0193	0.074	−0.0098	0.038
4	0.0160	−0.0063	0.036	−0.0035	0.019
5	0.0079	−0.0022	0.018	−0.0013	0.010
6	0.0039	−0.0008	0.009	−0.0005	0.005
7	0.0020	−0.0003	0.004	−0.0002	0.002
8	0.0010	−0.0001	0.002	−0.0001	0.001

class limits defined by $2^{i/2}$ ($i = -\infty, \ldots, -2, -1, 0, +1, +2, \ldots, +\infty$) or, in other words, for a grade scale in which the class interval is $\phi/2$ in Krumbein's notation.

By means of equations (1) it is possible to express the frequency of the jth size class among the whole grains in terms of certain thin-section size frequencies:

$$\begin{aligned} F(r_0) &= W_0 Q_0 , \\ F(r_1) &= W_0 Q_1 + W_1 Q_0 , \\ &\vdots \\ F(r_j) &= \sum_{k=0}^{j} W_k Q_{j-k} . \end{aligned} \tag{2}$$

The W_k are constants given by

$$W_0 = \frac{1}{T_0},$$

$$W_k = -W_0 \sum_{g=1}^{k} T_g W_{k-g}, \qquad (k \neq 0).$$

Equations (2) are used for reconstructing the true size frequencies from thin-section observations.

Since it is convenient to distinguish theoretical parameters of populations from empirical values of these parameters, the observed thin-section and reconstructed frequencies will be identified by prime signs, i.e., by Q_i' and $F'(r_j)$. The distinction is important in retaining a mental grasp of the situation. For example, $F'(r_j)$ has a standard deviation, but $F(r_j)$ does not. Furthermore, the mean value of the empirical frequency may not be equal to the theoretical parameter, in which case the observed value is termed a "biased" estimate of the parameter.

If Q_i is thought of as a relative frequency, the probability is Q_i that in any one of the N independent thin-section measurements the measured particle is placed in the ith size class. Hence NQ_i' is binomially distributed, and the variance of the relative frequency is

$$\sigma^2\{Q_i'\} = \frac{Q_i - Q_i^2}{N}.$$

Since $F'(r_j)$ is a linear function of the Q's, its variance is given by the general variance law for linear functions of random variables (Arley and Buch, 1950):

$$\sigma^2\{F'(r_j)\} = \sum_{k=0}^{j} W_k^2 \sigma^2\{Q'_{j-k}\} + 2\sum_{k=0}^{j-1}\sum_{g=k+1}^{j} W_k W_g \operatorname{Cov}\{Q'_{j-k}, Q'_{j-g}\}. \qquad (3)$$

The term $\operatorname{Cov}\{Q'_{j-k}, Q'_{j-g}\}$ is the covariance of Q'_{j-k} and Q'_{j-g}, which is known to be $-Q_{j-k}Q_{j-g}/N$ (Uspensky, 1937; David, 1951). Formula (3) therefore reduces to

$$\sigma^2\{F'(r_j)\} = [W_0^2 Q_j + W_1^2 Q_{j-1} + \ldots + W_j^2 Q_0 - (W_0 Q_j + W_1 Q_{j-1} + \ldots + W_j Q_0)^2]/N. \qquad (4)$$

By means of equations (1), this may be written as a function of the reconstructed size frequencies:

$$\sigma^2\{F'(r_j)\} = \frac{\sum_{k=0}^{j} V_k F(r_{j-k}) - F^2(r_j)}{N}. \qquad (5)$$

The constants of this expression are given by

$$V_k = \sum_{g=0}^{k} W_g^2 T_{k-g}.$$

Since the relative frequency $F_L'(r_j)$ of the jth size class found in counts of unsectioned grains is known to be an unbiased, efficient estimate of $F(r_j)$ (Arley and Buch, 1950), with variance

$$\sigma^2\{F_L'(r_j)\} = \frac{F(r_j) - F^2(r_j)}{N}, \qquad (6)$$

the ratio of formula (6) to formula (5) may be taken to express the efficiency of thin-section size measurements:

$$\text{Eff.}_{\text{T.S.}} = \frac{F(r_j) - F^2(r_j)}{\sum_{k=0}^{j} V_k F(r_{j-k}) - F^2(r_j)}. \qquad (7)$$

This relation shows that the efficiency of thin-section mechanical analysis is always less than 1 and that it tends to decrease from the coarse to the fine end of the size spectrum. The efficiency is zero for all classes j ($j > 0$) which contain no particles.

Before proceeding, it would be well to apply formulas (5)–(7) to a concrete situation. This has been done for the reworked glacial sand originally analyzed by Krumbein, whose data are reproduced in Greenman's paper. The theoretical relative frequencies of the logarithmic size classes were obtained by plotting the cumulated arithmetic class frequencies of Krumbein's whole-grain count on semilogarithmic paper, drawing a smooth curve through the points, and reading off the cumulated frequencies at 1.41 mm., 1.00 mm., 0.71 mm., and so on. The theoretical standard deviations of the relative frequencies obtained in repeated whole-grain and thin-section analyses of a sand with the assumed size distribution were found by arbitrarily assigning to N the value 300 and taking the square

roots of formulas (6) and (5), respectively. The results of these calculations, as well as the results of the application of formula (7), and the reciprocal of formula (7) multiplied by 300, are shown in table 2.

That classes containing no particles should have a standard deviation when reconstructed according to Greenman's method is readily understood by referring to equations (2) and making the substitutions $F(r_j) = F'(r_j)$ and $Q_{j-k} = Q'_{j-k}$. Since the Q'_{j-k} are random variables, their values will rarely be such as to make $F'(r_j) = 0$ when $F(r_j) = 0$. This shows that when the theoretical reconstructed relative frequency is zero, or near zero (perhaps 0.05 or less for a count of 300 particles), the Q'_{j-k} will often have such values that $F'(r_j)$ becomes negative. Since this result is physically inconceivable, it must be adjusted to conform to the observer's sense of propriety. However, it is easily shown that the mean value of $F'(r_j)$ obtained by Greenman's method is equal to $F(r_j)$ for all values of N, provided that the weights W_k are correct. Unadjusted $F'(r_j)$ is therefore an unbiased estimate of $F(r_j)$; any actual or potential adjustment introduces a bias. The net result is that the ultimate consumer of the data must use biased estimates for which no correction is possible. Nevertheless, it is possible to reduce the bias to a negligible level by combining all reconstructed classes near the fine end of the size range into one large class for which the probability of getting negative results is very small. This compound class would be known as the class of all "particles smaller than ———," its lower limit remaining undefined. The expression for its relative frequency, corresponding to equations (2), is

$$\begin{aligned} F(r_{j+1}) + F(r_{j+2}) + \ldots = {} & Q_{j+1} \\ & + Q_{j+2} + \ldots + Q_j(W_1 + W_2 + \ldots) \\ & + Q_{j-1}(W_2 + W_3 + \ldots) + \ldots \\ & + Q_0(W_{j+1} + W_{j+2} + \ldots). \end{aligned} \tag{8}$$

Index j identifies the finest size not incorporated in the compound class. If $\sum_{g=1}^{\infty} F(r_{j+g})$ is represented by $F(r_l)$, $\sum_{g=1}^{\infty} Q_{j+g}$ by Q_l, and $(W_{k+1} + W_{k+2} + \ldots)$ by U_k, equation (8) is more briefly stated as

$$F(r_l) = Q_l + \sum_{k=0}^{j} U_k Q_{j-k}. \tag{9}$$

The variance of $F'(r_l)$ becomes

$$\sigma^2\{F'(r_l)\} = \frac{F(r_l) + \sum_{k=0}^{j} R_k F(r_{j-k}) - F^2(r_l)}{N}, \tag{10}$$

in which the R_k are constants. This expression also permits the variance of any number of cumulated frequencies to be calculated.

It should be noted here that because $(W_0 + W_1 + W_2 + \ldots)$ must equal 1, Greenman's statement, "The values of $F(r)$ thus found will, in general, total to a little more than 100 per cent, largely because the thin-section distribution . . . will deviate somewhat from the theoretical distribution," cannot be true. Since each observed thin-section relative frequency is multiplied by the factor 1, the sum of the reconstructed relative frequencies must equal 1. The fact that Greenman uniformly obtains greater

TABLE 2

COMPARISON OF THE THEORETICAL PRECISIONS OF THIN-SECTION AND WHOLE-GRAIN MECHANICAL ANALYSES OF REWORKED GLACIAL SAND

Class Index	Whole-Grain Number Frequency* (Per Cent)	Standard Deviation† (Per Cent)		Efficiency† of Thin-Section Mechanical Analysis (Eff.t.s.)	300‡ / Eff.t.s.
		Thin-Section	Whole-Grain		
0	1.0	0.7	0.6	0.71	423
1	4.5	1.5	1.2	0.66	454
2	24.0	3.2	2.5	0.60	500
3	49.0	4.3	2.9	0.45	667
4	19.0	3.9	2.3	0.33	908
5	2.5	2.6	0.9	0.12	2500
6	0.0	1.7	0.0	0.00	∞
7	0.0	1.2	0.0	0.00	∞
8	0.0	0.8	0.0	0.00	∞

* Krumbein's data adjusted to fit logarithmic scale.

† It is assumed that 300 particles are counted in both thin-section and whole-grain mechanical analyses.

‡ This is the number of particles which must be measured in thin section to equal the precision obtained by measuring 300 unsectioned grains.

values merely signifies that his constants are not calculated with sufficient precision. The deviation $Q_i' - Q_i$ has nothing to do with it.

There remains the practical problem of deciding how many reconstructed classes are to be included in the compound class of all particles below a given size. Although this is perhaps largely a matter of personal judgment, an orderly procedure is suggested by the following reasoning:

Let it be assumed that several hundred particles have been measured in thin section, so that the application of normal law concepts could not be considered grossly unjustified. Let an arbitrary measure of bias be established such that, when the theoretical parameter $F(r_t)$ is so small that negative values of $F'(r_t)$ are obtained in more than π per cent of the repeated experiments, the observed frequency is considered objectionably biased. In practice, the occurrence of negative values about two and one-half times out of a hundred would seem to be a reasonable level of admissible bias. Accordingly, any reconstructed compound class with a frequency

$$F(r_t) < 2\sigma\{F'(r_t)\} \qquad (11)$$

should be incorporated in a larger class. Now, although both sides of relation (11) are totally unknown, we may utilize the fact that

$$\begin{aligned} F(r_t) + Ds\{F'(r_t)\} &= F'(r_t) \\ &= Cs\{F'(r_t)\} \end{aligned} \qquad (12)$$

to find the "probability" that

$$F(r_t) < 2s\{F'(r_t)\}. \qquad (13)$$

Here the estimated standard deviation, $s\{F'(r_t)\}$, is obtained from formula (10) by inserting the observed values of the reconstructed relative frequencies and taking the square root; C and D are numbers. Suppose $C = 4$. The probability that statement (13) is true is then the probability that $D \geqslant 2$, and we may say, with 97.5 per cent of confidence, that $F(r_t)$ is greater than $2s$. However, when $C = 4$ and when statement (13) is true, s will tend to be somewhat greater than σ. To compensate for this effect, we establish the rule of thumb that $F'(r_t)$ should exceed about $3.25s$–$3.50s$ in order to insure unbiased estimates at about the 95.0–97.5 per cent confidence level. It is possible that the recommended range of factors, 3.25–3.50, provides an unnecessarily large margin of safety, but a more precise evaluation of the confidence level associated with a given factor must await the solution of what appears at this writing to be a difficult problem.

The practical implications of the theory outlined above appear to be as follows:

1. Mechanical analysis of sectioned grains by Greenman's procedure is inefficient in a statistical sense. This means that more particles must be counted in thin section than would have to be counted in direct measurements of unsectioned grains in order to obtain results to a given order of precision. Moreover, the efficiency of thin-section mechanical analysis tends to decrease substantially from the coarse to the fine end of the size spectrum. The reconstructed data for the coarse sizes, up to the first peak of the size frequency curve, probably compare not too unfavorably in precision with the results of direct measurements, but after the first peak the relative precision may be poor. Thus an adequate delineation of the form of a polymodal frequency curve will probably require many more measurements than the observer would be accustomed to make if he were analyzing unsectioned grains.

2. The form of the frequency curve near the fine end of the size range will be obscure, no matter how many measurements are made in thin section. It is apparently impossible to identify the finest size class.

3. The necessity of interpreting the data physically implies that the ungrouped estimates for the finer sizes cannot be used without the ultimate introduction of more or less significant bias. This situation can be corrected satisfactorily by combining all reconstructed classes near the fine end of the size range into one large class containing all particles below a given size. As a practical and safe rule for determining how many classes are to be thus incorporated, it is suggested that the relative frequency of the compound class be at least 3.25 times, and preferably 3.50 times, its estimated standard deviation, $s\{F'(r_t)\}$. In symbols,

$$F'(r_t) \geqslant (3.25 \leftrightarrow 3.50)\, s\{F'(r_t)\},$$

$$\begin{aligned} s\{F'(r_t)\} = [&F'(r_t) - F'^2(r_t) \\ &+ R_0F'(r_j) + R_1F'(r_{j-1}) + R_2F'(r_{j-2}) \\ &+ \ldots + R_jF'(r_0)]^{1/2}/N^{1/2}. \end{aligned}$$

The $F'(r_t)$ are reconstructed relative frequencies, index t denoting the compound class, index j the finest size not incorporated in the com-

pound class, index $j-1$ the next larger size, and index 0 the coarsest size in the sample. Values of the R's, which are constants, are given in table 1 for a grade scale in which the class interval is $\phi/2$ in Krumbein's notation; N is the total number of particles measured. The same principle holds in some degree for all sizes except the coarsest. The estimated standard deviation of the relative frequency of any reconstructed class j other than the compound class is

$$s\{F'(r_j)\} = [V_0F'(r_j) + V_1F'(r_{j-1}) + \ldots + V_jF'(r_0) - F'^2(r_j)]^{1/2}/N^{1/2}.$$

Values of the constant V's are also given in table 1.

Although these conclusions are strictly true only when logarithmic grade scales are used, they obviously apply in principle when any other grade scale is employed.

This discussion is not intended to imply any criticism of Greenman's sound solution of the problem of mechanical analysis from thin-section data or to suggest that this type of mechanical analysis should not be attempted. It is, rather, the writer's intention to define the precision and basic limitations of the method for the benefit of those who may wish to draw scientific inferences from thin-section measurements of grain size.

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REVIEWS

Genesis and Geology: A Study in the Relations of Scientific Thought, Natural Theology, and Social Opinion in Great Britain, 1790–1850. By CHARLES COULSTON GILLISPIE. ("Harvard Historical Studies," vol. 58.) Cambridge: Harvard University Press, 1951. Pp. xiii+315. $4.50.

Geology was the first of the sciences to be more concerned with the *history* of nature than with the *order* of nature. In its period of early growth from 1790 to 1850, basic geological concepts were developed and modified in rather dramatic fashion, largely through the efforts of British scientists, who had a "peculiar love of regarding nature from a theological point of view." During these six decades geology was the most popular science in Great Britain, partly because the material was easily comprehensible, while its interpretation was highly controversial, and partly, perhaps, because it was an outdoor science and in its early days a uniquely individualistic one. Out of this background the development of geology provides an important study of the relations of scientific thought, natural theology, and social opinion.

In this historical treatment of the role of geology in the intellectual growth of Great Britain, Mr. Gillispie has clearly demonstrated that the many disagreements and dilemmas arose not from clashes *between* science and religion but from religion *in* science, from a religious attitude within geology, as well as from the fact that men of the church believed that their views needed the support of science. Most geologists of the period hoped that their studies would support a concept of a divinely created and supervised universe, and they took the scientific method to be a means of proving God's existence. As a result, scientific opposition was seldom distinct from theological opposition, a situation unlike that which prevailed during the vigorous debates about evolution and religion in later years.

The historical character of geology was responsible for the most disturbing problems faced by the early geologists. When the earth had been thought of as remaining unchanged since its creation, the question of the creator's control of events was not a very urgent one. When, however, nature was viewed as having a history and geology set out to piece together the record of successive events in the earth's past, then the issue of providential control became more difficult for scientists who wished their work to bear witness to the Deity's supervision. From the publication of Hutton's *Theory of the Earth* in 1795, every geological interpretation which marked a step forward touched off religious apprehensions and disagreements *among* geologists. And after each retreat the defenders of a providential view of nature took up new positions which their own researches were destined to destroy. The issue of Neptunist versus Vulcanist notions of the formation of the earth's crust introduced the question of the age of the earth. Application of the paleontological method of correlating strata led to a discussion of the antiquity of species. Enquiry into these matters led to doubts about Noah's deluge. Waning of a belief in the Flood was followed by the larger issue of the nature and cause of geological change, whether catastrophic or constant and gradual. Catastrophists attempted a final defense of the providential view of nature. But uniformitarianism prevailed, and this, in turn, led to Darwin's explanation, for, as a general concept of nature, uniformitarianism was carried to its logical conclusion in the idea of organic evolution.

Genesis and Geology is not a book about geology but about what geologists thought. It will not take the place of those detailed discussions of early geologists and their works found in well-known histories of geology. The geological items presented are not new, and most of the episodes have been described before. What is new and important is Gillispie's review and analysis of the ideas and controversies of those men responsible for the development of geology:

> Having decided to write about the opinions of scientists, I have not brought in anyone who was not a serious and productive naturalist, recognized as such at the time, and I have tried not to overlook any important British geologist whose work was relevant to the subject and who participated in the discussions I treat. . . . The attention they receive is proportional to the importance of their contributions to the con-

troversies in Geology, which is my subject, rather than to the importance of their contributions to science.

Gillispie has cited a wide range of criticism of the geological concepts discussed, but the basis for the criticisms is not always adequately developed. After presenting Lyell's uniformitarianism, for example, the author adds: "Geologically, of course, Lyell's critics were right. No one now holds such extreme views upon the uniform course of nature." Presumably, this is Gillispie's idea. Lest the reader accept this opinion as unanimous, he should know the closing sentences of the 1948 presidential address of the Geological Society of America: "*The uniformitarianism of Lyell seems not yet to require any of the amendments that have been suggested. . . . Long live Lyell and his doctrine of uniformitarianism!*" (Gilluly and James, 1949, Geol. Soc. America Bull. 60, pp. 561–590). Because this is a historical study, the text understandably contains many quotations and abundant notes. Unfortunately, this form may discourage the wide reading that the book deserves. An appended bibliographic essay on the pertinent literature will be an invaluable guide for students interested in the history of geology.

In order to set the stage for the early development of geological thought, the reader is introduced to the ideas and attitudes of some British scientists and philosophers of the late seventeenth and the eighteenth centuries. During the "heroic age of Geology" from 1790 to 1820, Neptunists and Vulcanists formulated their hypotheses of the origin of the earth's crust. Neptunists maintained that all crustal rocks had been precipitated from water. Vulcanists insisted that crustal rocks were of two kinds, one of igneous and the other of aqueous origin. Although the scientific inadequacies of the Neptunist notion were obvious to its critics, there were some significant attributes in its favor—its simplicity, its support of Noah's Flood, and no excessive demand on time. Consequently, most vigorous providentialists were Neptunists. The Vulcanist view offered no such advantages. Although the credibility of the Flood was not questioned, the belief that events in earth history resulted from the cumulative effect of minute forces and slight changes eliminated the necessity of divine intervention. It also implied a vast span of geological time. "We find no vestige of a beginning—no prospect of an end." Not only did Hutton fail to support a literal reading of Genesis, but some Vulcanists even maintained that it is not a scientist's responsibility to explain how God established the laws of nature.

During the declining days of Neptunism, William Smith had demonstrated his paleontological method of determining the correct succession of ancient strata. Yet more than a decade passed before his contribution received its deserved attention in geological thought. Meanwhile, the first generalization to be based on Smith's work was a theologian's contention that the fossil record established the veracity of Moses and demonstrated the regularity and order of God's handiwork. At this time the paleontological record was understandably assumed to be directed toward a particular goal, and there was generated a view that has haunted paleontology and prejudiced evolutionary interpretations down to the present under the name of "orthogenesis.

By 1820 Vulcanism was no longer widely disputed, and the fossil record had become an integral part of geology. In the decade that followed, British geological thought was dominated by Professor William Buckland, who had formulated a concept of catastrophism which bound geology to the explicit service of religion and supported the scientific soundness of the Bible. In the past, catastrophists believed, a series of causes different in nature from any now acting had molded the globe. Repeated revolutions of the crust, the lack of continuity between successive fossil assemblages, and Noah's Flood itself—the latest of the great catastrophes—were the result. Conybeare, Sedgwick, Murchison, and a host of amateur scientists of the period were ardent followers. In fact, the idea succeeded in winning for a time almost unanimous approval. And all who believed, accepted as proved the reality of the Flood and the recent creation of man—the diluvialist doctrine.

Lyell's masterful synthesis of geological knowledge in the early 1830's was devoted to the defense of uniformitarianism. In developing his argument, Lyell was led to deny the possibility of the universal deluge of the Scriptures, and, with the publication of *Principles of Geology*, few geologists continued to believe in the Flood. Thus catastrophism was deprived of its most popular catastrophe, and Lyell became the leader of an attack on the providential view of nature, leaving it only its last refuge, the creation of new species. For some years Lyell believed in special creations and the recent crea-

tion of man, but he later changed his mind and followed Darwin. Fundamentally, uniformitarianism was a kind of materialism—the uniformity of laws and materials of nature. If geology revealed a divine plan for the universe, it was one in which the laws of nature are immutable.

Uniformitarianism did not win immediate approval, but by 1840 it was widely accepted. Now scientific debate centered in the evolutionary development doctrine introduced by Chamber's *Vestiges of Creation*. Few men of note in Great Britain had any use for its crude evolutionary concept. Catastrophists and uniformitarians alike joined in repudiation. Of all Chamber's opponents, Hugh Miller—stonemason, able geologist, and romantic naturalist—was one of the most refreshing thinkers and damaging critics. Of all the geologists who set out to discover the divine plan of the universe, Hugh Miller "was the only one whose conception of divinity contained many elements of spirituality."

"In retrospect it is apparent that, although on the surface the problems raised by Vulcanism, Uniformitarianism, the *Vestiges*, and Darwinism are not the same, actually the pattern of reaction was a constant one throughout. Behind the discussion, therefore, was something more than always met the eye: the common tendency of all these theories to remove the hand of God from the course of events in the material world." But a large segment of British opinion was reluctant to accept from geology those findings which seemed to have this implication, and the diminishing importance of supernatural causation in earth history was accompanied by much more uneasiness in Great Britain than in other countries in the same period. In the concluding pages of his study Gillispie has attempted some analytical suggestions to account for these reactions, which, he finds, became a compound of physical science, providence, popularization, and patriotism.

The dilemmas of the early geologists may not seem so urgent as they once did. Few geologists today follow Adam Sedgwick and Hugh Miller in devoting their best efforts to the problem of integrating geological and theological concepts. Nevertheless, a geologist who believes that a significant part of understanding his science is a knowledge of its influence on social thought must be familiar with this episode in the history of science; he will find *Genesis and Geology* the most enlightening guide yet published. It is also an important contribution to an understanding of the history of evolution, for the progress of geology in the first half of the nineteenth century was an essential prelude to the formulation of a satisfactory theory of organic evolution. In a very real sense, James Hutton and not Lamarck was Darwin's intellectual ancestor.

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Principles of Geology. By JAMES GILLULY, AARON C. WATERS, and A. O. WOODFORD. San Francisco: W. H. Freeman & Co., 1951. Pp. viii+631; figs. 306. $5.75.

At the conferences on geological education held during the various geological society meetings in 1945, 1946, and 1947, the nature and present state of development of geology—the science of the earth—and the manner in which it could best be taught in colleges and universities were extensively reviewed. During these discussions a gratifying convergence of opinion was achieved on the proposition that, while the complex phenomena with which geology deals can be attacked at the initial level most effectively by the traditional natural-history methods, a higher level of attack must be based upon an explicit recognition of the physical and chemical nature of the phenomena dealt with. The training appropriate to these phenomena must therefore encompass not only the natural-history aspects of geology but also a foundation in basic physics, physical chemistry, and the necessary amounts of mathematics, all brought to bear on the problems of geology.

The prevalent geological training in colleges and universities, it was pointed out, has been confined largely to the natural-history phase, and even here the textbooks of general geology have become to a great extent stereotyped recitations of geological dogmas, with little regard for a distinction between observational data and inferences and the essential logic leading from one to the other. The need was therefore recognized for an extensive overhauling of the whole geological educational procedure, involving new viewpoints, new curriculum requirements, new standards of logical rigor, and *new textbooks*.

The book under review is one of the first texts of general geology to appear which have been explicitly written to meet the foregoing need. It is a textbook designed for beginning students of geology, usually Freshmen and Sophomores in

college, who may not have had prior training in college mathematics, physics, or chemistry. Consequently, where mechanical or chemical relations have been employed, an elementary explanation of the meaning of the concepts and symbols has usually been included.

In scope, the book emphasizes the physical aspects of geology, but it also includes a brief treatment of the biological aspects, a very good exposition of the principles by means of which geological history is deduced, and a broad outline of earth history from the Cambrian to the present.

The content of subject matter, as regards both inclusion and omission, and the sequence in which various topics are introduced are of particular interest. The first topic discussed is a fundamental one to the "science of the earth," but one that has long been neglected in geological textbooks, namely, the shape and size of the earth. In the present book these quantities are regarded as unknowns to be determined and are deduced by elementary methods from primary data. Logically, the next topic should have been the determination of the earth's mass and its mean density, which can easily be done by elementary methods. This, however, has been omitted entirely, although elsewhere in the text use of these quantities has been made.

After the earth's broad pattern, a chapter has been devoted to "Gravity, Isostasy, Strength." Then follow two chapters on earth materials—"Minerals" and "Rocks"—which, in turn, afford a basis for two more chapters on "Climates, Weathering, and Soils" and "Erosion." Then follows one on "Geologic Maps, Fossils, and Time." The historical approach is used, recounting early instances of geologic mapping in the Paris Basin and in England, involving observed areal and vertical distributions of sediments, correlation by means of fossils, and the deciphering of geologic history. This leads to the geologic time scale based on stratigraphy, which is then supplemented by an account of the determination of geologic time by means of radioactivity.

Next follow two chapters on earth crustal movements. Beginning with earthquakes and associated faulting and contemporary and geologically recent changes of elevation and warping, one is led easily to ancient earth deformation as indicated by folding, faulting, unconformities, and related structures.

The next eight chapters are devoted to a more thorough review of contemporary phenomena in the following order: "Downslope Movements of Soil and Rock," "Stream Erosion and Deposition," "Glaciers and Glaciation," "Ground Water," "Deserts," "The Oceans," "Igneous Activity," and "Earthquakes and the Earth's Interior." A chapter is then devoted to "Mountains," as representing one of the master-problems in earth phenomena. "Mineral Resources" are discussed in a final chapter, with particular emphasis upon their fundamental importance in human affairs.

Appendixes contain discussions of topographic mapping, the determination of minerals and rocks, and a table of atomic weights.

The distinctive character of the present work, however, is not indicated by an enumeration of the topics treated, since these are the traditional subjects of geology textbooks. It lies rather in the order and manner of treatment. Repeatedly, significant data—sometimes new, sometimes old—and methods of reasoning not commonly found in geology textbooks have been introduced. Also, throughout most of the book a conscious effort appears to have been made to present the evidence first, as a basis upon which to erect the principal inferences. The general result has been to convey the impression that geology is a young and active subject dealing with a complex array of phenomena, most of whose problems are still unsolved, rather than something that died about 1900.

The style is excellent, with a briskness and fluency that sustain interest and read easily. Particular comment is merited on the avoidance of the useless technical jargon which has long been the bane of geology textbooks. The authors have demonstrated that, by the use of plain English and a small number of well-chosen technical terms, it is possible to convey intelligibly almost any geological information. At the end of each chapter a few key references to published literature have been given.

The illustrations also are good. A total of somewhat more than three hundred figures, or about one figure to two pages, has been included. About a fourth of these are halftones of well-chosen photographs, and the remainder are line drawings, of which perhaps a third are based directly upon published figures in geological literature. In each case references and credit are given.

On the negative side, the treatment is by no means flawless, though many of its faults can easily be corrected in future editions by minor editing and revising.

Among the more serious items, the omission

of any discussion of the determination of the mass and mean density of the earth has already been mentioned. Also, in the chapter "Minerals," a chemical discussion involving such concepts as "protons," "neutrons," and "electrons" is introduced, which in the opinion of this reviewer serves no useful purpose. In fact, it is positively harmful, since it is unsupported except by authoritative assertion and creates an illusion of knowledge which a beginning student does not possess. It would have been far better to start with crystallographic observations, such as those of the pioneer crystallographers, and from these deduce an ordered interior arrangement.

The chapter "Rocks" is very good except for logical sequence. In this case the authors have followed the conventional procedure of asserting at the outset that there are three classes of rocks and specifying the mode of origin for each. Since the determination of the origin of the different classes of rocks has been one of the major achievements of geologic science, it is regrettable that the subject should not have been introduced with observational data and nongeneric terms and then, after appropriate reviewing of the evidence, arriving at the origin as a final result.

In discussing the mechanics of stream erosion, the energy that a stream must expend to carry its load of sediment downhill is considered. This is a familiar geological topic, but in the opinion of the reviewer its basis is anthropomorphic rather than physical. A stream's energy is completely dissipated whether or not a load is transported; the total energy is increased by a sedimentary load by the amount of the energy of the sediment.

The chapter on "Ground Water" is one of the best treatments of this subject which the reviewer has seen in a textbook of general geology and represents one of the rare cases in which Darcy's law has even been mentioned. However, Henry Darcy's name has been misspelled as "Henri Darcy," and the work attributed to him, while not fundamentally incorrect, is still about three or four times removed from what Darcy actually did and said. A passage based directly on the original work would have been preferable. Also, figure 14-7, showing the flow of ground water, is in error. This is based on a figure by Hubbert but has had a forked streamline added which was not in the original. This violates the conservation of matter.

The chapter on "Earthquakes" shows a typical seismogram with the *P*, *S*, and *L* phases. A graph is then shown of the arrival times of each of these phases, plotted against angular distance from the epicenter. As the curve for *L* is a straight line, it is correctly inferred that this represents a surface wave. The *P* and *S* curves are concave toward the distance axis, and from this it is concluded that these waves must penetrate the earth and increase in velocity with depth The increase of velocity with depth does not follow because travel-time curves concave to the distance axis will also occur for *P* and *S* waves of constant velocity.

The foregoing items are pointed out not as severe criticisms but rather as flaws marring an otherwise excellent treatment. The book represents a very definite advance from an earlier stage of geological science to a new one, and it merits wide acceptance. In the meantime, the field for still newer and better textbooks of geology on the elementary, as well as on the advanced, level is still open, and it is to be hoped that challengers will not be lacking.

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Symposium and Proceedings of Section F, Report of the 18th Session, International Geological Congress, Great Britain, 1948, Part 7: *The Geology, Paragenesis, and Reserves of the Ores of Lead and Zinc*. Edited by K. C. DUNHAM. London, 1950. Pp. 400; figs. 99.

This volume is a comprehensive review of the geology and resources of the lead and zinc deposits of the world. It contains thirty-four papers of variable length and completeness. Besides K. C. Dunham's Introduction, the book contains eleven papers on North America, one on South America, two on Australia, four on Africa, fifteen on Europe, and one on Asia. The volume has been considerably enlarged and enhanced from the earlier edition of 1948 by the addition of the opening and closing remarks of W. R. Jones, the chairman of Section F, thirteen additional papers, and discussions of the reports presented at the meetings. Excellent bibliographies accompany the editor's "Introduction to the Symposium" and most of the reports.

The Introduction is an important and useful contribution to our general knowledge of the world's lead and zinc deposits. The world's production and reserves of lead and zinc are pre-

sented in a concise summation of text, tables, and graphs, in which he has presented all the available, released statistics. His data indicate that average world lead production has not increased markedly since 1920. In contrast, zinc production has continued to increase, although at a diminishing rate, since 1920. The reserve data present a more favorable picture of both lead and zinc reserves than has been shown by previous estimates.

Dunham's discussion of the classification of lead and zinc deposits presents a new concept that "hypothermal lead and zinc deposits now occupy a predominating position," and it further points out that very few commercial deposits of lead and zinc ores belong to the epithermal class. He infers that the telethermal deposits, which have been a major source, will be of decreasing importance in the future because of less favorable possibilities for discovering new deposits.

However, in North America at least, a number of new discoveries, mainly the result of more detailed geologic work, have markedly increased the reserves of ore in the telethermal deposits of Virginia, Tennessee, southeast Missouri, Illinois, Wisconsin, and near Great Slave Lake, Northwest Territories, so that the total new reserves of ore developed in these deposits probably far exceed the new reserves developed in hypothermal deposits in North America. The probabilities are good that a continuation of the more detailed exploration methods in these telethermal districts will lead to other important new discoveries, contrary to Dunham's predictions.

In this brief review it is not possible to comment on all the papers in the volume. Several papers are merely brief reviews of the known geology and reserves of certain countries or districts. Examples of this type are the papers by Gonzalez Reyna on Mexico and Hsieh on China. They are very helpful in presenting general information on the location, geology, and reserves of the deposits in these countries. This information is of great potential value, as published descriptions of the deposits are commonly lacking or inadequate.

Among the remainder of the papers, all of interest, are several that the reviewer found particularly noteworthy. Probably the two outstanding papers that should be required reading for all students of ore deposits are: (1) "Lead and Zinc Deposits of the Cerro de Pasco Copper Corporation in Central Peru," by the geological staff of the corporation, and (2) "Ore Deposits at the Stantrg Lead-Zinc Mine" (Yugoslavia), by C. B. Forgan.

The Cerro de Pasco paper is a fine example of the impressive results produced by a geologic team working in a district of complex, related ore bodies and following closely the progress of active exploration, development, and mining. The large ore bodies, well exposed vertically and laterally at the surface and in mines, have yielded an unusually complete picture of hydrothermal mineralization, ranging from intense mesothermal to the low-intensity limit of leptothermal and even epithermal conditions. A marked concentric zoning is present in these deposits; this zoning is well illustrated at Casapalca. Here copper ores are most abundant in the central, inner zone and are surrounded by complex ores of zinc, lead, and copper, above which are epithermal silver ores containing argentite and ruby silvers and other sulfosalts, and laterally, on the fringes of the ore bodies, epithermal realgar, orpiment, and stibnite become abundant. The direct relationship of all the ore bodies to the local quartz monzonite stocks is demonstrated, although the sources of the solutions are shown to be the deeper parts of the stocks that were still liquid when the near-surface parts were already crystallized.

The paper on the ore deposits of the Stantrg mine is notable for the detail, completeness, and clarity of the geologic descriptions of the ore body and for the very clear, well-planned illustrations. The ore bodies are disposed peripherally about a dacite pipe of Tertiary age that is surrounded by a younger explosive breccia. The ore was deposited as replacement bodies along the bedding of limestones of Paleozoic age near their contacts with the breccia and with schists. Forgan quite clearly regards the early pyrite-magnetite-silicate stage of mineralization as pyrometasomatic, but, because the study was interrupted by the war, he was not able to determine the ultimate source of the ore. However, he states that the ore was emplaced during the final phases of igneous activity, after the consolidation of the pipe and at the end-stage of folding, while static conditions were being restored by local tensional adjustments. This paper is well worth reading, especially for the unusually clear presentation of the quantitative distribution of the ore metals and the relation of the ore to the controlling structures.

Other outstanding papers include the following subjects: a summary of the Sullivan mine in

British Columbia; the new data on the stratigraphy, structure, and mineralogy of the increasingly important Tennessee zinc district; the description of the central mining district of New Mexico; abundant new structural and ore-deposit data from the Taxco mining district, Guerrero, Mexico; a notable discussion of the huge Broken Hill, Australia, deposits situated in a local center of intense metamorphism and rock flowage; two papers on the deposits of Morocco and Tunisia, which should be of great value at the forthcoming meeting of the International Geological Congress in that area; a valuable contribution on the depleted telethermal replacement deposits of Poland; articles on the Mechernich-Maubach area of West Germany and on Kupferschiefer deposits, which have long been a subject of controversy, in which the syngenetic viewpoint of their origin is presented; a detailed geologic study of the Millclose mine in Derbyshire, England, which shows the value of careful geologic mapping just before abandonment of the mine; and two papers on the numerous complex lead and zinc deposits of Sweden.

Despite the lack of papers on several important deposits, notably those of Russia and Newfoundland, the volume is one of the most complete accounts of lead and zinc deposits in existence and is an essential reference volume for all students of metallic ore deposits.

ALLEN V. HEYL, JR.

U.S. Geological Survey
Washington, D.C.

COMMUNICATIONS AND ANNOUNCEMENTS

WYOMING GEOLOGICAL ASSOCIATION

The Seventh Annual Field Conference of the Wyoming Geological Association will be held August 1, 2, and 3, 1952. Headquarters will be in Thermopolis, and daily field trips will be conducted in the southeastern portion of the Big Horn Basin. Areas to be visited include the north flank of the Owl Creek Mountains, the Wind River Canyon (north portion), Mahogany Butte, Tensleep Canyon, and the Kirby Creek, Lake Creek, Black Mountain, Manderson, and Nowood anticlines. The general chairman is Dr. Andrew G. Alpha. Inquiries should be addressed to the Field Conference Committee, Wyoming Geological Association, P.O. Box 1168, Casper, Wyoming.

INDUSTRIAL MINERALS DIVISION A.I.M.E.

The fall regional meeting of the Industrial Minerals Division will be held in Chicago, September 3–6, 1952, concurrent with the fall meeting of the A.I.M.E. On September 3 and 4 there will be field trips to the Illinois Brick Company, Indiana molding sands at Dune Sand State Park, Standard Silica Corporation, and Illinois Clay Products Company. Technical sessions will be held September 5 and 6 and will emphasize industrial minerals of the Chicago area, building materials, and industrial ground water. Inquiries should be addressed to Mr. Robert C. Stephenson, Chairman, Fall Meeting Committee, Industrial Minerals Division, Pennsylvania State Geological Survey, Harrisburg, Pennsylvania.

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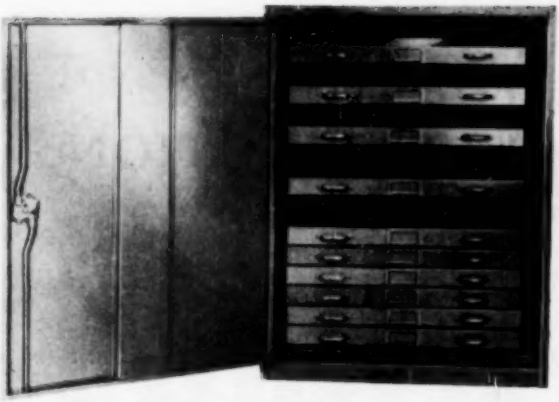

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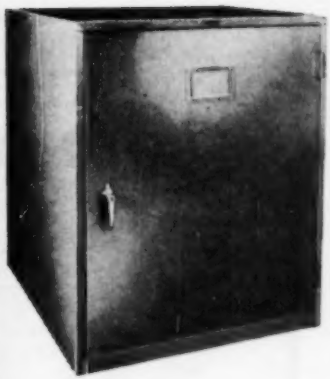

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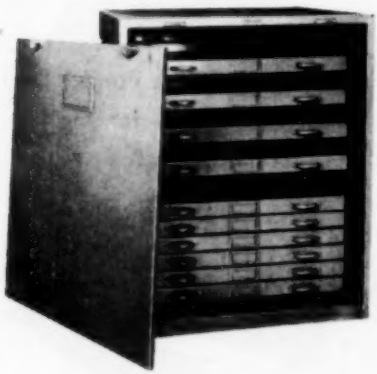

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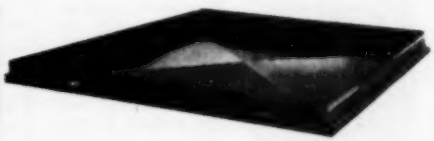

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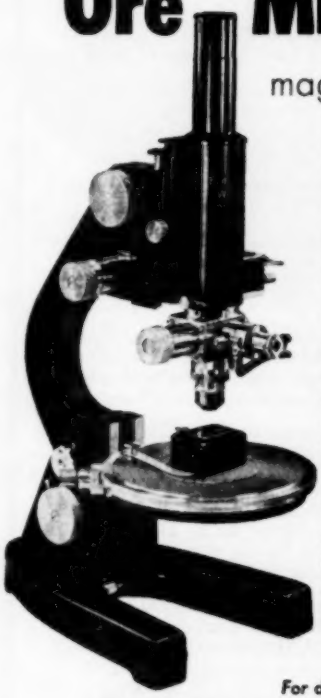

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